



University
of Glasgow

<https://theses.gla.ac.uk/>

Theses Digitisation:

<https://www.gla.ac.uk/myglasgow/research/enlighten/theses/digitisation/>

This is a digitised version of the original print thesis.

Copyright and moral rights for this work are retained by the author

A copy can be downloaded for personal non-commercial research or study,
without prior permission or charge

This work cannot be reproduced or quoted extensively from without first
obtaining permission in writing from the author

The content must not be changed in any way or sold commercially in any
format or medium without the formal permission of the author

When referring to this work, full bibliographic details including the author,
title, awarding institution and date of the thesis must be given

Enlighten: Theses

<https://theses.gla.ac.uk/>
research-enlighten@glasgow.ac.uk

**ENVIRONMENTAL FATE AND AN
ALTERNATIVE USE OF DINITROANILINE
HERBICIDE TRIFLURALIN**

ABDUL-SATTAR FARAJ KRAISH

B. Sc., Baghdad University, IRAQ, 1972

M. Sc., Alexandria University, EGYPT, 1980

Thesis submitted for the
Degree of Doctor of Philosophy
November, 1990

**Agricultural Food and Environmental Chemistry
(Pesticides)
Chemistry Department
Glasgow University**

ProQuest Number: 11007583

All rights reserved

INFORMATION TO ALL USERS

The quality of this reproduction is dependent upon the quality of the copy submitted.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if material had to be removed, a note will indicate the deletion.



ProQuest 11007583

Published by ProQuest LLC (2018). Copyright of the Dissertation is held by the Author.

All rights reserved.

This work is protected against unauthorized copying under Title 17, United States Code
Microform Edition © ProQuest LLC.

ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 – 1346

*To the soul of my mother who passed
away during the course of this work.*

ACKNOWLEDGEMENTS

I am extremely grateful to Dr. H. J. Duncan for his supervision and encouragement during the course of this work.

I also wish to thank Dr. I. M. G. Boyd for her valued assistance while the work was being carried out.

In addition, I wish to express my thanks to all members of staff and colleagues especially the technician Mr. M. Beglan.

I would like to extend my gratitude to Dr. W. Ritchie for providing facilities for a field experiment.

I acknowledge with thanks, receipt of a Research Studentship from the Ministry of higher Education and Scientific Research/IRAQ.

Finally, I extend my thanks to my father and all my family back home for their support as well as my wife and children for their patience and understanding during this study.

CONTENTS

	<u>Page No.</u>
ACKNOWLEDGMENTS	(i)
CONTENTS	(ii)
SUMMARY	(viii)
CHAPTER 1: INTRODUCTION	1
1.1 The need for pesticides	1
1.2 The need for environmental safety data	2
1.3 Laboratory model ecosystems to assess the fate and effects of pesticides in the environment	6
1.4 Entry of pesticides and its movement in the environment	8
1.5 Dinitroaniline herbicides and their fate in the soil environment	11
1.5.1 Volatilisation	13
1.5.2 Adsorption	15
1.5.3 Leaching	18
1.5.4 Uptake by plants and animals	20
1.5.5 Degradation of dinitroaniline herbicides in soil	23
1.5.5.1 Photodecomposition	26
1.5.5.2 Chemical decomposition	27
1.5.5.3 Microbial decomposition	29

1.6	Degradation of dinitroaniline herbicides in plants	34
1.7	Degradation of dinitroaniline herbicides in animals	37
1.8	Aims of the thesis	42
 CHAPTER 2: VOLATILITY OF TRIFLURALIN FROM SOIL		 45
2.1	Introduction	45
2.1.1	Volatility of dinitroaniline herbicides	45
2.1.2	Headspace analytical technique	52
	A- Headspace sampling	52
	B- Headspace analysis	60
2.2	Experimental	63
2.2.1	Chemicals	63
2.2.2	Soil-air flow model system construction	64
2.2.3	Tenax and Tenax trap preparation	67
	A- Tenax	67
	B- Tenax ability to trap trifluralin vapours	68
	C- Tenax trap preparation	69
2.2.3	Analysis of Tenax trap	72
	A- Headspace sampling	72
	B- Thermal desorption technique	72
	C- Heat desorption apparatus	73
	D- Gas Chromatography	74
	E- Retention time, linearity, and trifluralin recovery from the Tenax trap	76
	F- Effect of storage period on the recovery of trifluralin from Tenax trap under different conditions	76

2.2.5	Soil and soil treatment	77
2.2.6	Recovery of trifluralin from soil	79
2.2.7	Analysis of trifluralin residues in soil	80
2.2.8	Adsorption of trifluralin on soil	81
2.3	Results and discussion	84
	A- Headspace analysis	84
	B- Volatility of trifluralin from soil	87
CHAPTER 3:	PHOTODECOMPOSITION OF TRIFLURALIN	109
3.1	Introduction	109
3.2	Experimental	126
3.2.1	Chemicals	126
3.2.2	Irradiation	128
3.2.3	Photodecomposition rate assessment	130
3.2.4	Effect of some additives on the trifluralin photolysis rate	130
3.2.5	Photoproducts separation and identification	131
3.3	Results and discussion	132
CHAPTER 4:	AN INTRODUCTION TO POTATO SPROUT SUPPRESSANTS	155
4.1	The potato crop	155
4.2	Storage of potato	156
4.3	Sprouting	159
4.4	Sprout control	160
4.4.1	Storage temperature	160
4.4.2	Light	161
4.4.3	Irradiation	162
4.4.4	Natural sprout control	163
4.4.5	Chemical sprout suppressants	163

4.4.5.1	Chlorpropham and propham	164
4.4.5.2	Tecnazene	165
4.4.5.3	Maleic hydrazine	166
4.5	The case for using trifluralin as a sprout suppressant	167
4.6	Toxicology	173

CHAPTER 5: AN ASSESSMENT OF TRIFLURALIN FOR POTATO SPROUT

	SUPPRESSANT	178
5.1	Introduction	178
5.2	Experimental	179
5.2.1	Trifluralin preparation	179
5.2.2	Preparation of dust formulation	179
5.2.3	Potato treatments	181
5.2.4	Sampling for residues analysis and sprout growth observation	183
5.2.5	Growth test of trifluralin treated potato tubers	184
5.2.6	Analytical technique	185
5.2.6.1	Sample preparation for residues analysis	185
5.2.6.2	Extraction	186
5.2.6.3	Clean-up	187
5.2.6.4	Determination of trifluralin residues by GC	189
5.2.6.5	Recovery study	190
5.2.7	Wound healing	190
5.2.8	Potato box headspace	191
5.3	Results and discussion	192
5.3.1	Testing the stability of trifluralin on the solid carrier	192

5.3.2	Preliminary assessment	192
5.3.2.1	Trifluralin sprout inhibition	193
5.3.2.2	Trifluralin residue distribution within the tuber	196
5.3.2.3	A preliminary growth test with treated tubers	200
5.3.3	Assessment of different levels	203
5.3.3.1	Trifluralin sprout inhibition	203
5.3.3.2	Distribution of trifluralin residues within the treated tuber	205
5.3.3.3	Wound healing	207
5.3.3.4	Headspace of trifluralin in the potato box	208

CHAPTER 6: THE EFFECT OF TRIFLURALIN ON THE PREFORMANCE OF

	SEED POTATO TUBERS	209
6.1	Introduction	209
6.2	Experimental	212
6.2.1	Materials	212
6.2.2	Treatment of seed potato tubers	212
6.2.3	Airing	213
6.2.4	Planting	213
6.2.5	Experimental design	213
6.2.6	Emergence	214
6.2.7	Harvesting and grading	214
6.2.8	Residue analysis	214
6.3	Results and discussion	215
6.3.1	Residues	215
6.3.2	Sprouting and emergence	217
6.3.3	Yield	223

SUMMARY

This thesis can be divided into two major parts. The first was concerned with the environmental fate of the dinitroaniline herbicide trifluralin, in which the dissipation of this pesticide in the environment, in general, was reviewed and the two most important pathways of trifluralin dissipation were studied. These two pathways are volatility and photodecomposition (Chapters 2 and 3 respectively).

The study on the volatility of trifluralin from soil included the development of an analytical method suitable for the analysis of trifluralin in the treated soil headspace. The analytical method required the preconcentration of trifluralin vapours on an adsorbent trap (Tenax) followed by thermal desorption of the trifluralin vapours into a gas chromatograph to achieve a sensitive detection method. The Tenax trap was found to be very efficient at trapping trifluralin vapours with a high recovery which ranged from 92.3 ± 2.0 to 98.3 ± 1.4. The effect of storage conditions on the recovery of the trapped chemical was also investigated and it was found that the trapped sample of trifluralin could be stored at 5°C ± 1 for up to five days with no significant loss while on the other hand storage at room temperature (20°C ± 2) did cause a significant loss.

These measurements were carried out in a dynamic air flow soil system using three types of soils, a clay loam soil (Iraqi), a sandy loam (Arkleston, Scottish), and acid washed sand held at three differ-

ent moisture contents and two different temperatures. The results showed generally, that the total amount of trapped trifluralin from the sand treatment was much higher than from the Iraqi soil treatment and relatively less than from the Arkleston soil treatment compared with the Iraqi soil treatment under all investigated moisture contents and temperatures.

In addition, the volatility study included an adsorption assessment for trifluralin on the three soils investigated. The difference in adsorption was significant. The results of this assessment indicated that the soil organic matter content plays a significant role in the adsorption behaviour of trifluralin.

The photodecomposition study was set up to investigate the photolysis rate of trifluralin in various media water and different organic solvents. The effect of some additives on that rate was also concerned. In addition, an attempt was made to identify the possible photoproducts in water, methanol, and n-hexane.

The rate of trifluralin photolysis was more rapid in the n-hexane and less in methanol and distilled water and much less in acetonitrile. These differences may be due to the hydrogen donating properties of those different media since the reduction reaction is important in the photolysis of trifluralin.

In the case of the additives the crude chlorophyll extract exhibited the greatest effect in reducing trifluralin photolysis rate in methanol. The effect of other additives such as methylene blue and crystal violet was very close to the effect of the chlorophyll extract

while others had only slight effect. The effect of formulation on the photolysis rate was also assessed and a significant reduction was found in the rate of photolysis when the emulsifiable concentrate was exposed to the UV light compared with pure trifluralin.

Twelve trifluralin photoproducts were identified while another two were unidentified. Furthermore there were many bands isolated by TLC from which it was very hard to get very clean mass spectra. Three products were deduced as trifluralin photoproducts for the first time in this study.

The second part was to consider an alternative possible use of trifluralin as a potato sprout suppressant. The idea was born during the course of the first part of this study. The similarity of the two essential properties (volatility and mode of action) of trifluralin to the main sprout suppressant chemicals, chlorpropham and propham, lent support to this possibility.

A preliminary assessment was carried out at a level of application of 50 mg kg⁻¹ to assess the ability of trifluralin to suppress potato sprouting. In addition the assessment involved a growth test of treated tubers after an airing period of one month. Trifluralin successfully inhibited the potatoes from sprouting in long term storage (10 months) which compared favourably with chlorpropham. The growth test revealed that the inhibition of sprouting by trifluralin was reversible. These promising results led to a further assessment study to find the lowest effective level of trifluralin and the effect of trifluralin on the performance of treated seed potatoes.

When searching for the lowest effective level it was found that 10 mg kg⁻¹ application level was very effective at suppressing tuber sprouting until the end of the storage period of 31 weeks (at 10°C).

An analytical method for analysing trifluralin residues in treated potato tubers was developed for this purpose. The majority of the trifluralin was found in the tuber peel none being detected in the rest of the tuber (flesh).

A field trial was carried out to assess the effect of trifluralin on the subsequent performance of treated seed potatoes. No significant difference was noted, in the percentage of emergence after 42 days of planting time, between trifluralin treated tubers and untreated tubers using two cultivars. The results harvesting showed that the total yield of trifluralin treated tubers was not significantly different from that of untreated tubers while chlorpropham reduced the total yield by about half.

Further work needs to be done especially on a commercial scale of storage using suitable application methods such as fogging. This should be feasible. Also the toxicology of trifluralin needs further investigation as the trifluralin would be used directly on the potato tubers. However, accumulation of the trifluralin in the peel of the treated tuber should mean that the peeled tuber is trifluralin residues free.

CHAPTER 1

INTRODUCTION

1.1 THE NEED FOR PESTICIDES

Some 10,000 years ago men living in the Tigris /Euphrates valley moved from a hunting and food gathering way of life to a more settled existence in which food plants were sown and harvested. Extensive arable farming has only existed for the past five thousand years. The settled, however, can be followed with advantage by other consumers of the crops. Pests and diseases are those organisms which compete with man for his agricultural land. The ecological limitations which restricted their numbers in natural diverse vegetation are removed in the artificial crop environment and they emerge as pests, as a logical consequence of man's interference with nature. The control of pests and diseases is thus a problem as old as agriculture. History contains many references to seasons of high pest incidence, from the biblical plagues of Egypt to the failure of the Irish potato crop in the middle of the last century (Hill & Wright, 1978).

The use of agrochemicals has been increasing continuously since World War II. The use of herbicides has been expanding more rapidly than other pesticides (fungicides or insecticides). The total world sales of pesticides in 1978 was \$ 8.3 billion (Edwards, 1989). Somerville (1988) also reported that, pests worldwide are destroying about 35% of all potential food crops before harvest. These losses are primarily due to insects, plant pathogens, and weeds. After the crops

are harvested an additional 10 - 20% are destroyed by insects, micro-organisms, rodents, and birds. Total world-wide sales of pesticides in 1986 were estimated in terms of enduser value at \$ 17.4 billion, or in tonnage terms some 3 million tonnes.

The growth rate of world population is about 73 million people per year. In the year 2000, our globe will have a population of 6407 million people (Knusli, 1979), therefore, the need for more food and the control of human disease vectors will require even more use of pesticides which until now has played a more significant role than other tools in increasing food production and in saving man's life.

1.2 THE NEED FOR ENVIRONMENTAL SAFETY DATA

The marketing of pesticides throughout the world is controlled by official registration authorities and a condition of registration is the submission of satisfactory information upon toxicology and environmental impact. Information on possible metabolites in addition to the parent pesticide in a range of crops, soils, animals and aquatic environments are required as well. If early work in laboratory and small plot systems does not indicate unacceptable environmental problems, ecological investigations are extended to cover population studies on larger forms of life.

The toxicology evaluation of new pesticide starts with the measurement of the acute toxicity when administered by various routes to laboratory animals and is expressed as an LD₅₀ value. This is followed by the measurement of chronic toxicity by various sources, as in

food, when applied to skin and by inhalation. This procedure includes carcinogenesis and teratogenesis effects (Newman, 1978).

For new chemicals there are now well established schemes for the assessment of environmental risk before marketing and use can be approved. Basic environmental information on toxicity, persistence, and the actual use have to be provided to Government. The scale and the extent of the information base increases with the quantity of material to be sold or used. These data are used in the United Kingdom to assess the risks to human health by the Health and Safety Executive and the risks to the environment by the Department of the Environment (Otter, 1988).

In addition, for registration, data are needed that define clearly the importance of microorganisms as decomposers of the substances compared with other possible transformation reactions (nonsterile and sterile conditions) (Torstensson, 1980).

Microbial degradation studies are a rather unitary approach in a medium such as soil, with its heterogeneity of biological, chemical and physical phenomena. The information obtained is extremely limited. The properties of the products of pesticide degradation are usually considerably different to those of the parent, not only in biological activity, but also in toxicological, volatility and absorptive characteristics. It is thus important not only to know how much parent compound or total biological activity remains in soil or water, at intervals after pesticide application, but also to identify and quantify the products of degradation and where necessary, to investigate the properties of these products (Hill, 1978).

Mill (1980) reviewed that, EPA assesses the probable fate and effects of the chemicals if they are released into the environment. This information, combined with data on population exposure and release rates, should enable EPA to evaluate the probable hazard associated with commercial use of a specific chemical. Many environmental scientists now believe that the key to rapid, objective and reliable hazard assessment is the use of laboratory tests for fate and effects. Predictive tests for chemical fate or pathways can provide information on the concentration and location of a chemical and its products in a specific part of the environment as a function of time. Toxicological test methods give information on concentrations required to have some effect on a sensitive species in the same environment. Thus, together these data provide the basis for hazard assessment. In addition, it is possible using the chemical and physical properties of a new product, to visualize where in the environment the chemical will reside.

The basic process in any hazard evaluation involving the environmental effects of chemicals is to make predictions of the expected environmental concentration (EEC) and to match this with the experimentally determined no-effect level for appropriate environmental organisms. Once the data demonstrate that EEC is below the no-effect level, the product should be considered acceptable from an environmental point of view (Neely, 1980).

Since the United Nations Conference on problems of the human environment, which was held in Stockholm in 1972, studies on pollution and other environmental problems have been encouraged and supported in most countries, while the world organisations like FAO and WHO pay a

lot more attention to these problems in their planning than previously. However positive the general attitude of human beings towards the environment will develop in the future, the technical problems of how to predict environmental hazards of pesticides and how to find safer alternatives will still remain. The ability to predict pesticide hazards in general depends on a proper judgement of three different sets of parameters. Firstly those factors regarding the toxic properties of the compound like short and long-term toxicity, reproductive effects and mutagenicity. Secondly those concerning the fate of the chemical in the environment such as physicochemical behaviour, and biodegradability and thirdly the parameters which characterise the environment where the pesticide will be used, like the physiographical conditions, hydrology, biological diversity and life-cycle biology of important species.

A safer future with regard to the use of pesticides should not only be achieved by means of the development of new and more selective pesticides, a lot of improvement may also be accomplished by means of improved application and formulation techniques and by means of improved methods of pest and disease management like integrated and supervised control (Koeman, 1979).

The properties of a chemical that may need to be investigated include : 1- The physicochemical properties which would influence risks in the field or persistence as a residue. 2- Acute toxicity; LD₅₀ values by single doses and apparent mode of toxic action. 3- Skin penetration and absorption; percutaneous toxicity; irritancy of liquid or vapour to the body surface. 4- Cumulative effects of known function of LD₅₀ values over short periods representative of user exp-

osures. 5- Effects arising from prologed exposure, chronic toxicity. 6- Delayed effects, arising usually after a silent development period. 7- Metabolic studies. 8- Potentiation of, or by, other toxic chemicals under special circumstances. 9- Diagnostic and therapeutic possibilities (Fletcher & Kirkwood, 1982). In addition, they reviewed that, in order to measure possible accumulation in food chains a model ecosystem be created with plants, caterpillars, insects, small animals, fish, and radiolabelled pesticides to measure possible accumulation. Field studies are carried out on six metre square plots covering different soil types, in different parts of the country, to determine the effect of high and low concentrations of the pesticide on the soil microflora, soil microarthropods and earthworms using a variety of techniques. These tests may be continued over a number of years. Field tests are also carried out on wild birds using census methods.

Hopefully the techniques and results of this work will be useful, as a part of the information needs, in the worldwide concern about environmental safety.

1.3 LABORATORY MODEL ECOSYSTEMS TO ASSESS THE FATE AND EFFECTS OF PESTICIDES IN THE ENVIRONMENT

Laboratory model ecosystems or microcosms are potentially almost as diversified as the systems being modelled. Such systems range in complexity from petri dishes containing soil microflora and flasks containing microorganisms in water or nutrient medium, to elaborately constructed and instrumented terrestrial chambers, and computer-

operated model streams. A wide variety of them have been developed for rapid tests of the fate, transport and effects of pesticides, toxic substances and pollutants in general. Also they provide for "cradle to grave" regulation of the manufacture, transport, use, storage and disposal of all potentially toxic substances. These model systems are not a panacea, but are rather part of a logical framework that may offer a reasonable alternative to the accomplishment of a seemingly impossible task-the individual testing of each chemical covering all manner of tests and assays. Another significant facet of microcosm technology is that it stands intermediate between the laboratory, with its close investigator control yet lack of reality, and the field conversely beyond the control of the investigator and all too real. Thus microcosms offer several distinct advantages over conventional single-species testing at the laboratory bench, on one hand, and field trials on the other.

Microcosm technology has been applied to three main processes of chemical disposition transport-the movement of a chemical and its altered products between environment compartments; transformation-the nature and rate of formation of chemical and biological transformation products in various compartment of the environment; and bioaccumulation-accumulation of residues in the biota or biomagnification between trophic levels. In addition it has been used for other purposes such as the toxicological effects of chemicals and their transformation products in the environment on the organism, evaluation of chemical fate using various models of application and entry into the environment; behavioural effects on organisms, especially in food chains, evaluation of the interactions between chemicals in the environment; evaluation of biochemical mechanisms involved in comparative toxicology in

a variety of organisms; and screening for biological effect.

One of the critical deficiencies in microcosm systems to date has been the paucity of mathematical models as part of the systems. Such models would not only aid in interpretation of data and lead to improvements in experimental design, but they also provide a means of validating models of chemical fate, based upon physical chemical and biological laboratory data. More work must be performed to establish the validating and accuracy of these systems. Currently, microcosms serve best to clarify for further study in the field those questions which can not be answered under laboratory conditions (Gillett, 1980 and Metcalf, 1977).

In addition of the two articles which are very useful in reviewing and describing the design of a wide range of microcosms, Kraish (1980) reviewed 15 studies using various model ecosystems for a range of purposes and he used a terrestrial model ecosystem to investigate the fate of three different insecticides (mephosfolan, fenitrothion, and carbaryl) in soil, corn plant and percolated water.

In a part of this work (Chapter 2) an apparatus was designed to study the volatility of trifluralin in a dynamic manner to mimic the natural environment as near as possible.

1.4 ENTRY OF PESTICIDES AND ITS MOVEMENT IN THE ENVIRONMENT

Pesticides used in agriculture reach the soil environment by many direct and indirect routes. Some pesticides are applied dire-

ctly to the soil to control soil inhabiting pests, weeds, as systemics to control Phytophagous insects and systemic plant diseases, accidentally by spillage or disposal and indirectly by missing the target, run-off, death of the treated plants and animals, green manure, faeces from treated animals and deposit from amounts which remained airborne during application or volatilized from the treated surfaces. So the soil acts as a sink for all of these pesticides.

Most pesticide entry into the atmosphere comes from direct application such as from pesticide sprays for agricultural or public health purposes. Other sources are from industrial plants, fumigation of ships, aircraft and buildings or stores, burning of waste organic materials containing pesticide residues. In particulate or vapour forms at time of application, by volatilization after deposition on soil or adsorbed to wind-blown soil or plant particles. Air currents and wind result in rapid dilution of pesticides in air (Hill & Wright, 1978; Spencer & Farmer, 1980).

Pesticides enter into the aquatic environment directly as direct application for controlling aquatic weeds and algae, insects and snails or indirectly by drift from aerial or ground applications and movement via wind, water and soil erosion, spillage, accidents involving waterborne pesticide cargo, in domestic and industrial effluents and via migratory birds. Generally the quantities of pesticides entering natural waters indirectly are far less significant than those applied directly (Hill & Wright, 1978).

Pesticides volatilize from treated soil and plant surfaces and their vapours are transported away, often to distant locations by atm-

ospheric movement. Vapours in the atmosphere may be readsorbed by dry deposition and wet deposition and are brought to the soil surface by rain. Both the behaviour of dry and wet deposition and volatilization are all under the influence can be explained in terms of Henry's Law (Suntio et al., 1988).

In general, animals and plants which live in particular environment are exposed to pesticides either by direct application to control their pests or indirectly by many routes of contamination.

Movement of pesticides and their transformation products within one component of the environment (soil, water and air), or from one to other is not only a function of the chemical and physical properties of pesticides and the environment but also of the prevailing climatic conditions. In most cases, entry of a pesticide into one environment, whether soil, air, water, plants or animals, can lead to the redistribution of the chemical and its product into other component of the environment.

Distribution of a pesticide between soil, water, and air is controlled by many variables including temperature, soil properties, soil water content and its solubility, volatility and its degree of adsorption by soil constituents (Goring & Hamaker, 1972).

Pesticide may be lost from soil either by physical removal of unchanged molecule or by degradation. The physical removal occurs by volatilization, leaching and uptake by plants and animals. Degradation is possible in three ways, photochemically, chemically and biologically. The rate of pesticide degradation is related to its

distribution in the environment, chemical and physical properties of the pesticide, chemical and biological properties of the environment component, formulation, application method and climatic factors etc. Adsorption of pesticides to soil surfaces is a very important factor affecting pesticide biological and chemical degradation.

Many excellent reviews have been written discussing the topic of pesticide dissipation, in the soil environment by Hance (1980) and in various environments by Haque & Freed (1975); Hill & Wright (1978).

Since the dinitroaniline herbicide trifluralin, which is under investigation in this study, is mainly used as a soil incorporated pre-emergence herbicide, therefore those pathways of pesticide dissipation in the soil environment mentioned above will be discussed in some detail in the next section of this Chapter.

1.5 DINITROANILINE HERBICIDES AND THEIR FATE IN THE SOIL ENVIRONMENT

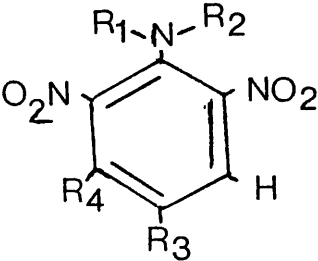
Dinitroanilines have been recognized as dye intermediates for several decades. The fungicidal activity of substituted dinitroanilines has been reported and the phytotoxic studies on bean plants were initially reported for 2,4-dinitroaniline in 1955. 2,6-dinitroaniline possessed a marked general herbicidal activity as compared to the 2,4-dinitro- or 2,3-dinitroanilines, with the latter being the least active of the three. Selective herbicidal activity was obtained by dialkyl substitution on the amino group of the 2,6-dinitroaniline molecule, with n-propyl the most active dialkyl substitution. Substitution in the 4 position of the ring resulted in herbicidal activity in

the following order: $\text{CF}_3 > \text{CH}_3 > \text{Cl} > \text{H}$. The first herbicide of this group was trifluralin [α, α, α -trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine], introduced by Eli Lilly in 1960. Trifluralin is the most prominent compound in the dinitroaniline series of herbicides (Table 1), which is used as a selective pre-emergence herbicide for controlling grasses and broad-leaved weeds in more than 40 crops. Most of dinitroaniline herbicides are used as preplant or preemergence soil-incorporation treatments. Trifluralin prevents the germination of susceptible weed seeds and prevents weed growth by inhibition of root development (Probst & Tepe, 1969; Klingman et al., 1975; Cripps & Roberts, 1978; Fletcher & Kirkwood, 1982).

In general the dissipation of the pesticides in the environment could have occurred physically by volatilization, leaching, adsorption and uptake by plants and animals or by degradation by chemical, photochemical or biological means.

In this section, these dissipation processes will be discussed. The discussion will be primarily concentrated upon the processes which are important for dinitroaniline herbicides and particularly for the fate of trifluralin.

Table 1 Dinitroaniline Herbicides

General Structure					
Common name	Substituents				
	<u>R₁</u>	<u>R₂</u>	<u>R₃</u>	<u>R₄</u>	
Trifluralin	C ₃ H ₇	C ₃ H ₇	CF ₃	H	
Benfluralin	C ₂ H ₅	C ₄ H ₉	CF ₃	H	
Nitralin	C ₃ H ₇	C ₃ H ₇	SO ₂ CH ₃	H	
Dinitramine	C ₂ H ₅	C ₂ H ₅	CF ₃	NH ₂	
Butralin	H	s-C ₄ H ₉	t-C ₄ H ₉	H	
Oryzalin	C ₃ H ₇	C ₃ H ₇	SO ₂ NH ₂	H	
Isopropalin	C ₃ H ₇	C ₃ H ₇	iso-C ₃ H ₇	H	
Dipropalin	C ₃ H ₇	C ₃ H ₇	CH ₃	H	
Fluchloralin	C ₃ H ₇	C ₂ H ₄ CL	CF ₃	H	
Profluralin	CH ₂	C ₃ H ₇	CF ₃	H	
Pendimethalin	H	CH(C ₂ H ₅) ₂	CH ₃	CH ₃	
Ethalfuralin	C ₂ H ₅	C ₄ H ₇	CF ₃	H	

1.5.1 VOLATILISATION

The atmosphere has been regarded as an infinite sink for pesticides. The volatilization of pesticides is a dynamic process in which

kinetics are important. The evaporation rate of a pesticide depends not only on its vapour pressure and the temperature, but also on air flow and the ratio of surface area to applied mass of the deposit (Hance, 1980).

Kennedy and Talbert (1977) concluded that dinitroaniline herbicides undergo increasing losses when applied under field conditions and incorporation is delayed. Losses may be increased further by high soil and ambient temperatures. In addition, Grover et al. (1988) reviewed that the field data have established volatilization and air transport as a major pathway for trifluralin dissipation in the environment. The vapour pressure of trifluralin (1.99×10^{-4} mm Hg at 29°C) suggests that volatility can be a factor under certain field conditions. When trifluralin was applied at $1 - 10 \text{ Kg ha}^{-1}$ to wet soil surfaces up to 4 Kg ha^{-1} were lost per day. The rate was a function of temperature (Probst et al., 1976).

Wheatley (1976) reported that incorporation into soil after application, greatly suppresses volatilization of trifluralin and other herbicides. In another study, Walker et al. (1982) gave an example to show, how it is important to incorporate the trifluralin into soil to reduce its loss by volatilization. When trifluralin was applied to the soil surface in the summer in an experiment in Maryland, 90% volatilized in 2 - 3 days, but in a similar experiment in Georgia where it was incorporated to 2.5 cm, losses were only 22% in 120 days.

Therefore, volatilization plays a significant pathway in dissipation of trifluralin from soil to the atmosphere. The volatilization of dinitroaniline herbicides, particularly trifluralin will be studied

in chapter 2 with a detailed introduction covering the theoretical and applied aspects of volatility and the analytical techniques of volatile compounds.

1.5.2 ADSORPTION

Adsorption is one of the important processes which influences the fate of soil applied pesticides. Adsorption-desorption phenomena occupy a central position in controlling the distribution of herbicides in soil. The distribution of herbicide between the liquid or gas phase and the adsorbed phase affects the phytotoxicity and selectivity of herbicides, their effects on non-target organisms and the risk of surface and ground water pollution.

Bailey and White (1964) reviewed and discussed in detail the factors influencing the adsorption and desorption of organic pesticides in soil directly such as soil or colloid type, physico-chemical nature of pesticide, soil reaction, nature of the saturating cation on the colloid exchange site, soil moisture content, nature of formulation, and temperature, whereas the physical properties of soil as a substrate and climate exert a more indirect influence.

Adsorption depends on many factors which often interact in a complicated way, such as molecular properties of the solute, soil constituents and climatic conditions. The properties of soil constituents and molecular properties of solute are complementary in controlling the adsorption of herbicides. Adsorption of herbicides varies greatly according to the nature of soil organic matter and is

greatly conditioned by the ionic composition of the clay surface. Mineral and organic soil constituents are not stable and undergo various transformations as they age. This situation, plus the fact that mineral and organic constituents are frequently associated, explains why it is difficult to predict soil adsorption behaviour simply from the gross soil composition. It is possible to describe adsorption-desorption phenomena with a Freundlich type equation.

Several workers have tried to establish a relationship between adsorption and water solubility. Beside water solubility, some other properties have been used by measuring partition coefficient between octanol or hexane and water or using reverse-phase thin layer chromatography (Hayes, 1976; Calvet, 1980). They gave also much fuller theoretical information about this topic.

Adsorbate-adsorbent bonds belong to two categories: 1- high energy bonds (>80 KJ / mole): ionic bonds, ligand exchange, 2- low energy bonds (<80 KJ / mole): ion-dipole and dipole-dipole interactions, hydrogen bonds and London-Van der Waal's bonds. Hydrogen bonds are mainly associated with N-H and O-H groups and N and O atoms so that all herbicide molecules are able to establish hydrogen bonds. Two kinds of hydrogen bonds have been described, (1) between adsorbed water molecules and adsorbed organic molecules, (2) between surface groups and organic molecules. The first type has been suggested as a mechanism for the adsorption on montmorillonite of carbamates and atrazine and the second has been proposed for a variety of systems. London-Van der Waal's bonds are due to dispersion forces and they probably exist with all herbicides. Hydrogen bonds are either directly between solute and adsorbent or indirectly through hydrated

water molecules. In addition, Hill and Wright (1978) reviewed that the adsorption is due to bonds both of the Van der Waal's type and to those resulting from electrical charge between the pesticide and the soil surface. The amount of organic matter is the most important soil characteristic affecting the adsorption of the majority of pesticides, although electrolytes and the negatively charged surfaces of clay particles play an important role in adsorbing many cationic pesticides. Bailey and White (1964) classified the adsorption as two general types, physical adsorption or Van der Waal's adsorption and chemical adsorption. The first is due to orientation or dipole-dipole interactions; polarization or induced dipole interactions; dispersion interactions, ion-dipole interactions in addition to repulsion interactions. The second is due to coulombic forces and results from bond formation between the adsorbent and adsorbate. A hydrogen bond may be classified under either physical or chemical adsorption, depending on whether the parameter of heat of adsorption or formation is taken as the major criterion for classification.

There are many methods which may have use in increasing the knowledge of herbicide-adsorbent interactions in model systems such as pure clays or pure organic materials. Absorption spectroscopy (IR studies are more numerous) and X-ray diffraction have been used to provide information about adsorbate-surface interactions.

Adsorption of pesticides to mineral and organic soil particles is mostly a reversible process and volatilization resumes when the soil is rewetted (Osgerby, 1973; Hill & Wright, 1978; Glotfelty et al., 1984).

The soil behaviour of trifluralin appears to differ in some aspects from the general rules for adsorption in soil followed by most neutral herbicides. Trifluralin was strongly adsorbed on organic matter but adsorption on kaolinite clay was similar to, or even more than on montmorillonite clay. Organic content of the simulated soils reduced trifluralin activity, and clay plus organic matter combinations appeared to be synergistic in reducing phytotoxicity (Hollist & Foy, 1971) whereas Bardsley et al. (1967) reported that the phytotoxicity of trifluralin increased in soil amended with organic matter.

Because the adsorption process is a very important factor affecting the fate and behaviour of pesticides in soil including dissipation of pesticide by volatilization, it was worth assessing the adsorption of trifluralin to the soils used in the trifluralin volatility study (Chapter 2).

1.5.3 LEACHING

Pesticides move in the soil solution both by diffusion and by bulk transfer involving a mass flow of water containing the pesticides. The downward movement of pesticide in solution through the soil profile in the zone above the water table, is termed leaching (Hill & Wright, 1978).

Knowledge of the movement of pesticides and their transformation products in soils or from other environments helps us to understand the performance of soil applied pesticides and other

pesticides which reach the soil by other routes against pests, safety of the crops and to evaluate the risk of leaching through the soil to ground water, and the runoff to the surface water and of the exposure of non-target organisms.

The movement of pesticides is controlled by the rate of water flow through the soil pores (microscope scale). Differences in flow rate result in the gradual spread of a pesticide band as it moves through the soil.

A fertile soil contains about 40% solid particles and 60% pore space. At field capacity, the smaller pores are filled with water and the larger filled with the air. The partition of pesticide between the three phases (soil, water, and air) in such a dynamic system as soil can help us to understand and predict the behaviour of pesticides in the field (Riley, 1976).

Pesticides can be lost from soil by leaching and surface runoff. The runoff does not appear to be a serious problem in practice. There are many factors controlling the leaching in the field such as the amount and nature of water movement through soil, adsorption, water solubility and rate of degradation. In addition, evaporation of water from the soil surface reduces downward movement (Bailey & White, 1964; Riley, 1976; Hill & Wright, 1978; Leistra, 1980).

The mobility of herbicides can be measured in leaching experiments using soil columns, with care to prevent the collapse of soil structure. The relative mobility can be estimated by soil-layer chromatography, using water as a mobile phase. Studies of the movement of

herbicides in soil under field conditions and by using a soil lysimeter are also illustrated (Rhodes et al., 1970; Brockman et al., 1975; Fadayomi & Warren, 1977; Leistra, 1980). In addition Rhodes et al. (1970) discussed also the relationship of the Freundlich isotherm constants to the R_f values.

Anderson et al. (1968) determined by bioassay of segmented soil columns the leachability in a clay loam soil of some dinitroaniline herbicides (trifluralin, benefin and nitralin). Their leachability varied even though their water solubility is the same (about 0.5 p.p.m.). Trifluralin and benefin were leached in relatively minute amounts (trifluralin slightly more than benefin) while nitralin and its breakdown product were leached to depth. In another study Probst et al. (1967) reported that no evidence was found about the trifluralin migration laterally or in depth in the soil plot.

As trifluralin is strongly adsorbed to soil organic matter and has low water solubility, the leaching process is not considered important in the movement of trifluralin in soil (Upchurch, 1966; Hollist & Foy, 1971; Horowitz et al., 1974; Klingman et al., 1975; Miller et al., 1975; Golab et al., 1979).

1.5.4 UPTAKE BY PLANTS AND ANIMALS

The uptake by plants is related to the ability of the plant to absorb the pesticide and to the availability of the pesticide for the plant. There are relatively few reports in the literature which clearly demonstrate that plants play an important role in the removal of

pesticides from soil (Hill & Wright, 1978).

Little is known of the extent of this process although a few examples, such as in the case of maize which is able to absorb and metabolize considerable quantities of simazine, are well documented (Walker et al., 1982).

In physiological terms, herbicides may move in a plant along pathways which are non-living (apoplast) or living (symplast) or both. Almost all herbicides show some symplastic movement since they must enter living material in order to be toxic.

Various factors, such as metabolic inhibitors, root aeration, soil type, water solubility, herbicide concentration, the presence of adventitious roots, PH and formulation all affect plant uptake (Zaki & Reynolds, 1961; Taleker & Lichtenstein, 1972; Fletcher & Kirkwood, 1982). In addition, there are direct and indirect effects of light, temperature, nutrient status and water on transport (Sagar et al., 1982). However Fletcher and Kirkwood (1982) reviewed that light and temperature (inhibitory) affected absorption of trifluralin by cells isolated from Zinna sp. and the entrance into the roots was greatly facilitated by breaks in the epidermis such as might occur from disease or mechanical damage.

The classical view that the roots are largely responsible for the direct uptake of herbicides from the soil has had to be modified by the knowledge that some soil-applied herbicides enter the parts of the shoot system that are underground. Direct entry into the shoot system may be of some significance with trifluralin because it has

appreciable volatility (Sagar et al., 1982).

Recently Vandeventer et al., (1986) concluded from a few reviewed studies that, substituted dinitroaniline absorption and translocation is herbicide-dependent and that more ^{14}C translocation is seen in susceptible than tolerant species. In addition, they studied the absorption, translocation, and metabolism of ethalfluralin and trifluralin to determine the basis for differences in response in two species of Solanum spp in nutrient solution. The absorption was greater for S. scabrum than for S. ptycanthum in the case of both compounds. More ^{14}C ethalfluralin than ^{14}C trifluralin was found in the shoots of plants of both species.

The absorption and translocation of the dinitroanilines has not been adequately investigated to enable any concrete conclusions to be drawn (Ashton & Crafts, 1973). Trifluralin or its degradation products are not readily absorbed from soil by variety of tolerant crops but the roots of plants grown in soil treated with trifluralin contain a residue in their outer shell (Probst et al., 1967). In addition, Ashton and Crafts (1973) reviewed much evidence to indicate relatively little absorption and translocation of trifluralin from root to shoot and vice versa. However, trifluralin was found in leaves, epicotyl, cotyledons, hypocotyl, and roots of peanut after applying trifluralin to various parts of peanut plants suggesting extensive translocation. Trifluralin may actually circulate in the plant's translocation systems (apoplastic and symplastic) and accumulate in areas of high lipid content, i.e., cotyledons (Kerchersid et al., 1969). Moreover, Stang and Rogers (1971) observed a little movement out of the soybean roots, and limited movement of radioactivity into the leaves of cotton, appa-

rently via the metaxylem. Radioactivity accumulated in the protoxylem of cotton stem where many elements appeared to be plugged.

Depending on theoretical and practical available data, it seems that the dissipation of trifluralin from soil through uptake by plants is mostly extremely small and has no environmental significance.

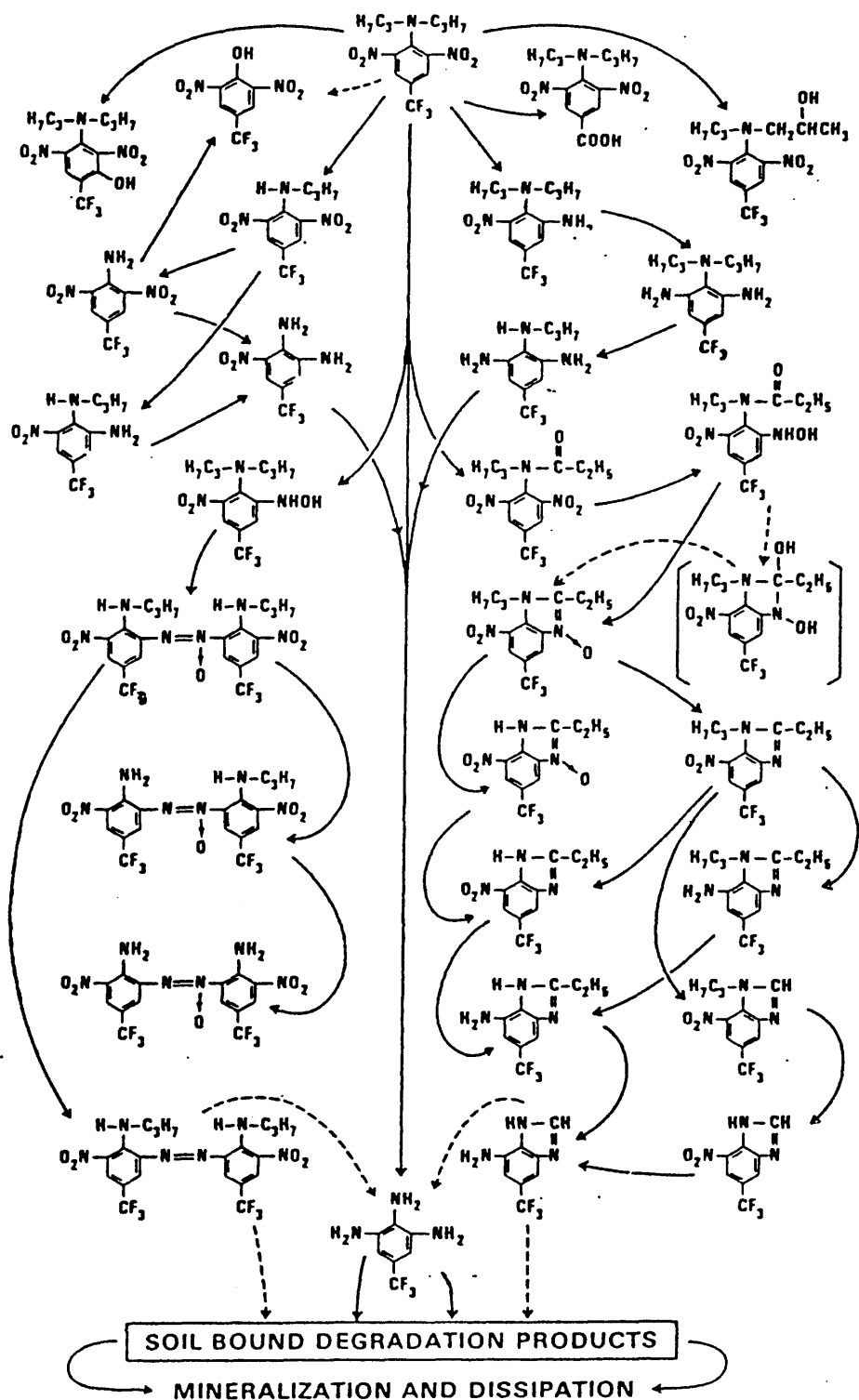
There is no available literature concerning the uptake of trifluralin by animals but generally speaking, since the trifluralin is a soil incorporated herbicide, the invertebrates in soil are capable of moving pesticides, whether in their tissues or on their outer surfaces over relatively small distances. When invertebrates contaminated with pesticides are eaten by mammals or birds the distances over which the pesticides are transported can be increased enormously.

1.5.5 DEGRADATION OF DINITROANILINE HERBICIDES IN SOIL

The soil environment acts as a sink for pesticides, which reach soil by various ways. Mostly the dinitroanilines are incorporated directly into the soil. Whilst on or in soil, as mentioned previously (1.5), the pesticides in general are subjected to physical dissipation and transformation. The physical dissipation may occur by volatilization, leaching, uptake by plants or animals and adsorption. The process of adsorption does not actually cause loss of pesticide from soil but cause a loss in availability of pesticide in soil solution. The volatilization and adsorption are the most important dissipation processes for trifluralin and other dinitroanilines while the other physical dissipation mechanisms such as leaching and uptake by plants

Fig.1.1 Postulated pathways of trifluralin in soil.

(→) Most likely route. (--->) Possible alternative route (Golab et al., 1979).



and animals are not important.

Soil is a complex biological and chemical medium. The kinetics of adsorption and desorption might affect rates of loss by controlling availability for degradation. The activities of soil microorganisms may vary with time depending on the availability of nutrients and other energy sources, and there may be competing reaction sequences within the degradation process (Hurle & Walker, 1980).

The rate of transformation of pesticides in soil is dependent on many factors including pesticide chemical structure, formulation, rate and method of application, soil type, distribution in soil, repeat treatment, cropped soil, combination with other pesticides, nutrient status, PH, moisture content and temperature, although other reagents such as nucleophiles, reducing agents and oxygen may also be involved. Free radical reactions may degrade pesticides, the biota in the soil may in part be responsible for the generation of these free radicals, for example, via hydrogen peroxide produced by microbial extracellular oxidase enzymes (Probst et al., 1976; Hill & Wright, 1978; Hurle & Walker, 1980; Fletcher & Kirkwood, 1982).

The transformation or degradation of pesticides may be either by non-biological or biological means. Walker et al., (1982) reported that, degradation is possible in three ways, photochemically, chemically or enzymatically and different steps may be performed by different mechanisms. It can be difficult to decide which mechanism operates in a particular instance because the same product can often be formed in two or three ways.

1.5.5.1 PHOTODECOMPOSITION

The majority of pesticides are susceptible to photodecomposition under experimental conditions, although usually the maximum rate of breakdown occurs at wavelengths rather shorter than those which reach the soil from the sun (290 - 450 nm). Photochemical effects probably occur mainly prior to soil entry (in the atmosphere or on plant surfaces) and also occur on the soil surface but to a lesser degree. The importance of the photodecomposition process in the field is problematical, although it may prove to be significant in some cases, e.g. with some substituted dinitroanilines (Wright & Warren, 1965; Hill & Wright, 1978; Walker et al., 1982).

Crosby (1976) and Probst et al. (1976) reviewed many studies about trifluralin photodecomposition and the possible loss of trifluralin by photodecomposition was suggested.

As mentioned previously, trifluralin is a volatile compound. In other word, volatilization is the main route of trifluralin dissipation to the air from soil after soil application. So the importance of the photochemical decomposition process on the trifluralin vapour phase is the key factor affecting the fate of trifluralin in the environment. Hence the air environment rather than other compartments will be much more important.

The rate of trifluralin photodecomposition in different media, alone and with some additives, and the attempted identification of its photoproducts will be the subject of trifluralin photolysis in chapter

3. Whereas the photolysis in air will not be part of the work it will be discussed through available literature because this work needs special equipment which is not available in the time.

1.5.5.2 CHEMICAL DECOMPOSITION

A variety of mechanisms, dealkylation, reduction, oxidation, hydrolysis, cyclization and combinations of these, are involved in the transformation of dinitroanilines in soil result in the formation of more than 30 degradation products. The dinitroaniline herbicides degrade in a similar pattern with few exceptions, and only minor differences are observed. There is no indication of a buildup of any of the transformation products in soil, and none has ever been found at a concentration greater than 4% of the original amount of herbicide applied. Dinitroaniline herbicides degradation in soil is affected by aerobic and anaerobic conditions. The aerobic pathway proceeds by a series of oxidative dealkylation steps whilst the anaerobic pathway is initiated via a sequential reduction of the nitro groups. Cyclization involves both oxidation and reduction. The difference in the nature of the degradation products formed by the aerobic versus the anaerobic pathway is more quantitative than qualitative, thus, reduction also occurs under aerobic conditions and oxidative dealkylation under anaerobic conditions. Whereas under anaerobic conditions, reduction of nitro groups predominates (Miller et al., 1975; Probst et al., 1976; Golab et al., 1979).

Golab et al. (1979) investigated the degradation of trifluralin in soil under natural conditions over a 3-year period, to characterize

further the transformation products formed under both field and laboratory conditions, and to obtain information on the nature of the nonextractable soil-bound products. They isolated and identified 28 transformation products (Figure 1.1) in these studies. None of the isolated transformation products exceeded 3% of the initially applied trifluralin. After 3 years the 0 - 15 cm soil layer contained 43.5% of the applied radioactivity. Less than 1.5% of the applied trifluralin could be detected in soil, 4% was distributed among numerous transformation products, and 38% remained as soil-bound residues (α,α,α -trifluorotoluene-3,4,5-triamine). The trifluoromethyl group of trifluralin remained intact through the various transformations of the compound, except for the formation of 4-(dipropylamino)-3,5-dinitrobenzoic acid and 3,5-dinitro-4-(propylamino)-benzoic acid in which the trifluoromethyl group was oxidized to the carboxylic acid. The final fate of the trifluoromethyl group is most probably mineralization to fluoride. Aromatic hydroxylation of trifluralin and its transformation products may facilitate rupture of the benzene ring leading to the eventual mineralization and dissipation of trifluralin degradation products. It is possible that the degradation products which result from the cyclization (benzimidazoles) and the azoxy compounds may also result in formation of α,α,α -trifluorotoluene-3,4,5-triamine.

Brewer et al. (1982) and Wheeler et al. (1979) reviewed that, volatility and chemical decomposition appear to be the primary modes of dissipation of dinitroaniline herbicides in soil. The dissipation was much more rapid under flooded conditions than in soil maintained at field capacity. The rate of trifluralin degradation appears approximately to double with 10°C increases in temperature from 10 to

40°C. In addition, Brewer et al. (1982) found in a field study, a similar trend, more dissipation of trifluralin in flooding condition and the dissipation was much slower at 40°C than reported for trifluralin at 10 or 15°C.

In general trifluralin when incorporated into soil at an agricultural application rate showed moderate persistence. No evidence of differences in soil residue levels could be related to the number of times the chemical had been applied. Trifluralin does not accumulate with repeated annual applications (Paraka & Tepe, 1969; Savage, 1973; Carter & Caper, 1975; Kearny et al., 1976; Zimdahl & Gwynn, 1977; Smith & Muir, 1984).

1.5.5.3 MICROBIAL DECOMPOSITION

The major and often the only mechanism by which such compounds are converted to inorganic products is biological. Incomplete degradation is frequently of environmental concern because the products of these particular reactions may be more toxic than the parent compound, whereas the parent molecule was nontoxic, more persistent than the parent compound or subject to biomagnification or other biological changes different from those undergone by the precursor molecule (Alexander, 1980).

Microorganisms are responsible for numerous transformations that cycle elements and energy in nature. Microbial transformations with different underlying biochemical mechanisms are the main route of chemical disappearance from soil. Rate and route of degradation is la-

rgely controlled by the environmental factors, agricultural techniques, the properties of the pesticide and pesticide combinations, losses by volatilization, uptake by plants or animals and adsorption effect, the rate of microbial degradation indirectly by reducing the available amount of pesticide for microbial transformation. Complex adsorption phenomena between microorganisms and soil particles, local differences in the concentrations of hydrogen ions and nutrients at the surfaces of soil colloids lead to different microsites with respect to aeration. Microbial population exists in a dynamic equilibrium formed by interactions of abiotic and biotic factors that can be altered by modifying environmental conditions. Microorganism are able to degrade a wide variety of chemicals, from simple polysaccharides, amino acids, proteins, lipids, etc to more complex materials such as plant residues, crude oils, waxes and rubbers (Hill, 1978; Torstenson, 1980; Haider, 1983). The degree of degradation varies from compound to compound. Some molecules can be utilized as sole sources of carbon, nitrogen and energy for the growth of a particular organism leading, in some but not all cases, to the complete metabolism of the substrate while others are particularly degraded to non-metabolizable products and some are apparently completely resistant to microbial attack. Some microorganisms metabolize the pesticide molecules in the presence of alternative substrates (Cripps & Roberts, 1978; Hill, 1978).

Torstenson (1980) inferred that the initial microbial disappearance of pesticide is slow or absent (lag phase) but increases progressively with time and reaches a steady state (usually a logarithmic rate of change) for a period of time. It is deemed likely that the herbicide is used as microbial substrate. Future applications of the

pesticide may be transformed more rapidly, either with or without a reduced lag phase. The same information was reviewed by Audus (1960) about the kinetics of the microbial transformation processes. During the lag phase the microorganisms produce degradative enzymes followed by an enrichment phase when the adapted microorganisms multiplied, using the substrate as the preferred energy source.

The absence of a lag phase does not necessarily indicate the presence of constitutive enzymes but may be due to cometabolic transformation of the pesticide. The alternative substrate from which the organism obtains its growth and energy source already being present in the environment (Hill, 1978). The co-metabolism (with no lag phase) has been found for long persistence herbicides while the initial lag phase behaviour has been found for short persistence herbicides in soil (Walker et al., 1982).

Most of the microbiological degradation studies are usually carried out with pure cultures of isolated microorganisms, with mixed microbial populations such as those which occur in soil and with cell-free extract or purified enzyme systems (Cripps & Roberts, 1978; Hill & Arnold, 1978). However, the metabolic activity of any microorganism in laboratory media may not be reflected in nature, because of either poor competitive ability of the organism, or adverse environmental conditions (Hill & Arnold, 1978).

The principal reactions involved in pesticide metabolism of most organic compounds include α -oxidation, oxidative dealkylation, thioether oxidation, phosphorothionate oxidation, epoxidation of carbon-carbon double bonds, hydroxylation, aromatic ring cleavage, hy-

hydrolysis, dehalogenation, nitro-reduction, condensation and conjugate formation. The numbers, types of substituents and the positions of linkage of side chains onto aromatic rings can also affect the reaction rate. Hydrolysis, reductive dechlorination and nitro-reduction may be enhanced in flooded state, dehydrochlorination and ring cleavage are less favoured (Hill, 1978).

Probst et al. (1967 & 1976) and Cripps and Roberts (1978) reviewed many studies about the metabolism of trifluralin in soil and pure cultures. Trifluralin in soil under aerobic conditions metabolizes to several metabolites resulting from dealkylation and reduction reactions and form in small amounts but the evidence suggests that they are shortlived and convert into polar products. These polar products appear to be the result of strong binding of anilines to the soil since an aromatic triamine is formed upon strong chemical reduction. Under anaerobic conditions, the rate of degradation is more rapid and reduction reactions predominate and precede dealkylation (Probst et al., 1967).

Parr and Smith (1973) found evidence to show that the initial degradation of trifluralin in soil was microbiological under anaerobic conditions. The evidence was that, the degradation of trifluralin was enhanced in the presence of an organic substrate and the compounds were stable in moist, anaerobic soil after autoclaving. However, Messersmith et al. (1971) observed that only 3.5% of the radiolable was evolved as $^{14}\text{CO}_2$ in ten months. The higher rate of degradation of trifluralin in waterlogged soil was confirmed.

In many studies reviewed by Probst et al. (1976), some of papers

considered that the breakdown of trifluralin by soil microorganism accounts for only a small fraction of the total dissipation. Thus microorganisms may contribute to the destruction of trifluralin to simpler compounds, but the evidence does not suggest that this is the major mode of degradation. The other studies showed that dinitroanilines were degraded into the corresponding mono- and didealkylated derivatives compound and 2,4-dinitro-6-trifluoromethyl-m-phenylene-diamine. The cyclized (benz-imidazole) product was identified also. α,α,α -trifluoro-2,6-dinitro-p-cresol derived from trifluralin and benefin. The hydroxylation of isopropalin was observed in the isopropyl group resulting in the formation of a new degradation product, α,α -dimethyl-3,5-dinitro-4-dipropylamin-obenzyl alcohol.

More recently Haider (1983) reviewed that, the typical transformations, observed in aerobic soils include N-dealkylation and benzimidazole formation. Bound residues in the humic and fulvic acid fractions of soil organic matter gradually build up. Trifluralin and similar herbicides are lost much faster from anaerobic soil than from relatively aerobic soil. Major products from both trifluralin and benefin, under such an environment, are derived from the reduction of one or two nitro groups and/or dealkylation of the N-alkyl groups. At redox potentials below about +100 mV in a flooded soil the nitro groups of trifluralin are rapidly reduced. In aerobic soils, especially when they were wet and contained organic nutrients, this reduction was also observed. Thus it is possible that more of the reduced compounds are formed and a substantial portion of them was bound in soil humic or fulvic acids.

1.6 DEGRADATION OF DINITROANILINE HERBICIDES IN PLANTS

In addition to the fact that plants play a role in the dissipation of pesticides in the environment, there is another reason to discuss this topic since the herbicide trifluralin will be under consideration as a potato sprout suppressant, (see Chapters 4,5, and 6) and will be in direct contact with the potato tuber, it is therefore a very important reason for discussing this aspect in this literature section. In addition there is no published work available on residues and metabolism of trifluralin in potato tubers, so it seems desirable to understand fully the fate of trifluralin in plants in general.

There are many ways plants can be exposed to pesticides, direct treatment, spray drift, uptake from the soil, and particle deposition on plant surfaces.

The degradation of herbicides by plants is an important mechanism of detoxification generally minimising the possibility of transmission of the compound through food chains and acting as an important basis for selective toxicity. The degradation may result from a wide range of chemical reactions, most of which are catalysed by specific enzymes though a few appear to be non-enzymatic in nature. The following types of reactions have been shown to be involved in herbicide degradation in higher plants: oxidation, decarboxylation, deamination, dehalogenation, dethioation, dealkylation, dealkyoxylation, dealkythiolation, hydrolysis, hydroxylation, conjugation with plant constituents, and ring cleavage. By a combination of chemical processes the original herbicide molecule may be degraded completely to innocuous

substances such as carbon dioxide, water and ammonia (Fletcher & Kirkwood, 1982; Sagar, et al., 1982). Fletcher and Kirkwood (1982) also reviewed that the degradation processes (in soil) include oxidation, N-dealkylation, cyclization and nitro group reduction; certain of these mechanisms have been reported to occur in plants and dealkylation has been reported too.

Harvey (1983) classified the metabolism of pesticides in plants broadly as free compounds, conjugates and bound residues. Free compounds and conjugates are both extractable from plant tissues, although conjugates are generally more polar than most free compounds and are generally soluble only in water or other highly polar solvents.

Herbicides are often applied much earlier in the growing season than other crop protection chemicals, thereby reducing the chances of significant levels of residues remaining in the crops until harvest. Herbicide level declines due to degradation on or in the treated plant also they can be lost by volatilization, photodecomposition or leakage in solution from plant tissues, or shedding of mature or killed leaves containing herbicide or dilution resulting from plant growth (Sagar et al., 1982).

As noted previously (Section 1.5.4) the absorption and translocation of the dinitroaniline herbicides is not well understood, Ashton and Crafts (1973) reported that the molecular fate of these compounds in higher plants is not well understood either. However most of the studies reviewed by Probst et al. (1967), Probst and Tepe (1969) and Probst et al. (1976) indicate that the evidence available is inadequate to claim that trifluralin and other dinitroanilines are actively

metabolized by plants. There is similarity of products in plants and in soil. Except for the metabolite 4-dipropylamino-3,5-dinitrobenzoic acid which appears to be exclusively a higher plant product since it has not so far been found in soil degradation studies.

The extensive studies of trifluralin, benefin, nitralin, dinitramine, isopropalin and oryzalin reveal conclusively that these dinitroanilines and their degradation products observed in soil do not accumulate in the edible portions of crops tolerant to the action of these herbicides except for certain root crops such as carrots.

The major metabolite of trifluralin in plant is α,α,α -trifluoro-2,6-dinitro-N-propyl-p-toluidine which appears to form as a result of dealkylation. Two minor metabolites are also formed by processes involving reduction and dealkylation in one case and oxidation in a other. Two routes of degradation have been proposed which are believed to operate simultaneously. Dealkylation and reduced derivatives of trifluralin have also been detected in extracts from peanut and sweet potato (Golab et al., 1967; Biswas & Hamilton, 1969). Hatzios & Penner (1982) reported the reduction of aromatic nitro groups to corresponding amines as a minor pathway in metabolic studies with dinitroaniline and nitro-substituted diphenyl ether herbicides and it is believed to be enzymatically catalyzed by aryl nitroreductases. In addition, Biswas and Hamilton (1969) identified another two phenolic metabolite derivatives and a benzoic acid derivative of trifluralin through the utilization of infrared spectroscopy in crude sweet potato and peanut extracts.

Recently contradictory informations compared with early studies

has been found by Vandeventer et al. (1986). They studied the absorption, translocation and metabolism of ^{14}C ethalfluralin and ^{14}C trifluralin in two species of Solanum using treated nutrient solution to determine the basis for differences in response by these two species to those dinitroaniline herbicides. Plants of S. scabrum absorbed more ethalfluralin and trifluralin than plants S. ptycanthum. More ethalfluralin than trifluralin was found in the shoots of plant of both species. 72 h after treatment with herbicides, the conversion to water-soluble metabolites was greater for ethalfluralin than for trifluralin. In the shoots of plants from both species an average of nearly 55% and 40% of the ^{14}C recovered was found in the water-soluble fraction following ethalfluralin and trifluralin treatments respectively.

In summary-based on the above literature, trifluralin and other dinitroanilines, which are poor in absorption and translocation, are degradable and metabolize into water-soluble metabolites in higher plants.

1.7 DEGRADATION OF DINITROANILINE HERBICIDES IN ANIMALS

As an attempt is being made to develop a new use for trifluralin, as a potato sprout inhibitor as part of this thesis, an attempt should be made to consider directly its role in the human food chain. That reason this gives more necessity to the main purpose of this section which is the fate of trifluralin in animals as a part of the environment.

Animals can receive pesticides directly by both deliberate application and accidental contact or indirectly by eating treated or contaminated plants or other animals. The possibility that the pesticides and their metabolites reach man either through the food chain or other exposure is well known.

Degradative reactions of pesticides in general may involve hydrolysis, oxidation, reduction and rearrangement. Generally, but not always, compounds may be degraded via the same pathways in plants and in animals and it has been shown that the reactions are mediated by similar enzymes in both plants and animals. Conjugation is the most interesting type of reaction during the degradation process, whereby the organism combines the pesticide, or its derivative with a normal constituent of the organism to synthesize a new compound which is more readily eliminated from an animal, or bound into an inactive form in plant. Metabolism of pesticides usually results in detoxification, although in some cases into a more active or toxic form (Harvey, 1983).

However, the trifluralin metabolism pathway is a reductive degradation in ruminant animals, artificial rumen fluid, and rumen bacteria. Trifluralin in monogastric animals undergoes both oxidative and reductive pathways of degradation (Probst et al., 1976). In addition artificial rumen fluid rapidly degrades trifluralin and benefin to less than 1% in about 12 h (Golab et al., 1967; 1970). Probst et al. (1976) reviewed that, under the same conditions, isopropalin and oryzalin were degraded in about 24 h and 30 min, respectively. In other study the mixture of rumen fluid and artificial saliva incubated in an atmosphere of CO₂ and 37°C incubation, degraded trifluralin and

benefin rapidly with the formation of the major metabolites of trifluralin, mono and dinitro group reduction products. The monodealkylated derivative and the reduced monodealkylated derivative were observed too. A decline of these metabolites precedes an increase in polar products.

Eighty percent of the trifluralin radioactivity was excreted in the feces while the remaining portion appeared in the urine after feeding a single dose to rats. Trifluralin and the amino derivative of trifluralin were isolated and identified from feces. Three urinary metabolites were isolated and identified as the dealkylated product, the diamine and the reduced monodealkylated derivative while other minor metabolites were detected in trace amounts. Trifluralin metabolism in the dog is similar to that observed in the rat (Emmerson & Anderson, 1966).

Examination of urine, feces, blood, and milk of a lactating cow which was fed at 1 and 1000 p.p.m. for 39 and 13 days, respectively revealed detectable residues only in feces. Trifluralin, one metabolite with one and other with two nitro groups reduced, respectively were detected in the feces by gas chromatography. The result indicate that trifluralin was rapidly metabolized (Golab et al., 1969). They also fed trifluralin to a goat at 1 p.p.m. for different times, 99% of administered radioactivity was accounted for within 6 days (17.8% in the urine and 81.2% in the feces). Neither urine nor feces contained trifluralin. The major metabolite found in the urine and the only one in feces was trifluralin with both nitro groups reduced. Other minor metabolites in urine were detected all indicating a reductive pathway of trifluralin degradation in ruminant animals. Golab

et al. (1970) found similar results with labeled benefin. In addition, Probst et al. (1976) reviewed many studies, in which nitralin was rapidly excreted (52% in urine and 47% in the feces) after feeding nitralin to rats. When cows were fed nitralin at 50 p.p.m. in their ration, no detectable residues of nitralin or its metabolites were found in milk, feces and urine. Examination of the extracts of urine from rats fed isopropalin indicated, a similar metabolic pathway to that of trifluralin, the monodealkylated and didealkylated metabolites of isopropalin were observed with unidentified products.

Williams and Feil (1971) found that only two rumen bacteria degraded trifluralin in rumen fluid from 12 characterized rumen bacterial strains. These bacteria are Bacteroides ruminicola subsp. brevis (GA-33) and Lachnospira multiparus (D-32). Similar metabolites were identified as mentioned before. No loss of the trifluoromethyl group or cleavage of the ring of trifluralin was observed. Trifluralin degradation by rumen bacteria generally follows the pathway outlined for anaerobic degradation in soil.

The artificial rumen fluid system degraded benefin faster than trifluralin and both reduction products of benefin were formed with other minor metabolites which were associated with the anaerobic benefin degradation in soil. The polar metabolites of benefin constitute 79% of the extracted radioactivity after 16 h while approximately 45% in the case of trifluralin was polar products. Reduction of the polar mixture with tin hydrochloric acid yielded a mixture containing a major portion of reduced dinitro didealkylated compound (Golab et al., 1969). Williams and Feil (1971) found the polar products which they obtained could be reduced as well. They concluded that polar pr-

oducts were not likely to be azo compounds as suggested by Golab et al. (1969; 1970), since they are readily degraded by rumen microorganisms (Katz et al., 1969).

Probst et al. (1976) reported that the azo compounds are possible under anaerobic as well as aerobic conditions, although no current conclusive evidence for this has been reported in the literature and there are no reports till now on the formation of the cyclization of dinitroaniline to benzimidazole compounds by rumen bacteria or in ruminant animals. They reviewed just one study about the formation of benzimidazole compounds in artificial rumen fluid.

Kaufman (1976) reviewed that the reduction of nitro groups is common to a number of aromatic nitrosubstituted pesticides including the dinitroaniline herbicides. It is well known that when aromatic nitro compounds such as trinitrotoluene or dinitrophenol are administered to animals, the corresponding amino, hydroxylamino, and azoxy compounds are excreted in the urine.

Paulson (1975) reviewed many studies, about trifluralin and benefin metabolism in animals. Thier results suggested that a low degree of absorption depending on the fact that the feces are the primary route of elimination of trifluralin and/or its metabolites. He concluded that the metabolism of trifluralin and benefin has apparently not been investigated in avian species and information concerning the fate of these compounds in mammals is not complete. Some of the nonpolar metabolites in feces and urine have been identified. These make up only small part of the metabolites in excretory products. The nature of the polar metabolites and nonextractable metabolites have not been

reported.

As noted in the literature above, trifluralin apparently is metabolized in animals by reduction of the nitro groups and removal of the N-alkyl groups. The other possible metabolism pathways such as cyclization, condensation (to form azo, azoxy) and altered trifluoromethyl group are not extensively studied. In addition the polar metabolites are not identified either. This field needs more investigated to, confirm some of the observations made and to carry out proper animal tests.

1.8 AIMS OF THE THESIS

Trifluralin is a herbicide which used worldwide under quite different environmental and climatic conditions. Some times in hot weather there is a need to double the recommended application rate to get sufficient weed control. It is important to investigate the influence of selected environmental factors on its fate in the environment. Since the fate and dissipation of trifluralin in the environment is mostly affected by two processes, volatilization and photodecomposition, these two important processes will be investigated as part of this thesis.

On the other hand due to the physical (volatility) and biochemical (mode of action) properties of trifluralin which are similar to the current used potatoe sprout inhibitors, propham and chlorpropham, an attempt will be made to develop an alternative use for the herbicide trifluralin in the new field (potato storage).

From above short introduction of this section, the course of this thesis has two aims:

1- A study in the environmental fate of the dinitroaniline herbicide, trifluralin which includes an investigation into the most important dissipation processes, volatilization and photodecomposition. The volatilization study involves first, a development of an analytical method for the volatile compound trifluralin. The method contains a sampling technique, sample storage and thermal desorption technique using gas chromatography for quantitative analysis. Secondly involved is a dynamic air flow soil system with different soils, moisture contents and temperatures.

The purposes of the photodecomposition study are to assess the photolysis rate of trifluralin in various media, including the effect of some additives on the photolysis rate and also to identify possible photoproducts in different media.

This part of the work will be carried out in 2nd and 3rd Chapters of this thesis.

2- An alternative use for trifluralin as a potato sprout suppressant. The idea of behind this arose after work on the first aim had been started and during the literature survey. A similarity was found in the physical property (volatility) and the mode of action (cell division inhibitor) of trifluralin and the common potato sprout suppressants, propham and chlorpropham. These two factors supported the possibility of an alternative use for trifluralin as a potato sprout

inhibitor, which is very essential in this field. This part of the work will be carried out in 4th, 5th, and 6th Chapters. The 4th Chapter will be an introduction to the trifluralin alternative use

CHAPTER 2

VOLATILITY OF TRIFLURALIN FROM SOIL

2.1 INTRODUCTION

2.1.1 VOLATILITY OF DINITROANILINE HERBICIDES

Volatilization is a process of change of phase, a condensed phase such as a liquid or solid may be transformed into vapour by elevation of temperature or reduction of external pressure. If the substance moves directly from the solid phase to the vapour phase without an intermediate liquid phase, the process is known as sublimation. The tendency of an organic compound to volatilize is expressed by its vapour pressure (Plimmer, 1976).

Pesticides range in volatility from fumigants, such as gaseous methyl bromide, to herbicides with vapour pressure below 10^{-8} mm Hg. The volatility of different compounds is a relative value, being ultimately dependent on the vapour pressure, and varies with temperature, water solubility and adsorption characteristics. However the same physical and chemical principles govern their rates of volatilization regardless of inherent potential volatility. Potential volatility is related to vapour pressure of the pesticide, but actual volatilization rate will depend on environmental conditions and all factors that modify or attenuate the effective vapour pressure of a pesticide. Vaporization from surface deposits depends only on the vapour pressure of the chemical and its rate of movement away from the evaporating surf-

ace. Vaporization from aqueous systems depends not only on the vapour pressure of the chemical but also on its water solubility; vaporization from soil is controlled by water solubility, adsorption, vapour pressure, formulation, transformation products, plant cover, wind and relative humidity, rate of application, soil temperature and moisture content. In addition to the factors directly affecting vapour behaviour of the chemical in the soil, the loss to the atmosphere will depend on the resistance of the chemical to degradation and leaching (Parochetti & Warren, 1966; Goring & Hamaker, 1972; Kenaga, 1972; Spencer et al., 1973; Plimmer, 1976; Wheatley, 1976; Hill & Wright, 1978; Spencer & Farmer, 1980).

Adsorption is a function of soil, as well as herbicide properties. Soil adsorption characteristics of non-ionic substances are reasonably well predicted by their octanol:water partition ratio (P) using the relationship : $\log Q = 0.52 \log P + 0.62$ where Q is given by $100 K / \% \text{ organic matter}$, K being the soil water partition ratio (Hance, 1980). Hance (1980) reported also that, temperature influences vapour movement because of its effects on vapour pressure. The response usually follows the relationship $\log_{10} P = A - B/T$ where A and B are constants, T is the temperature and P is the vapour pressure.

Diffusion provides one of the mechanisms for movement of pesticides through soil, a consequence of random molecular motion as a result of which material moves from a higher to a lower concentration, in accordance with the second law of thermodynamics. Vapour phase diffusion in the soil is controlled by the same factors that control vapour pressure such as temperature, adsorption, soil water content, plus in addition soil porosity, hence bulk density, the tortuosity of soil

pores and the number of blocked pores (Hance, 1980).

The evaporation rate of a substance is determined solely by its vapour pressure, or vapour density, and its rate of diffusion through the air closely surrounding the substance. Volatilization from deposits on inert surfaces or from any accumulation of a chemical is controlled by the saturation vapour density or vapour pressure of the chemical and its rate of movement away from the surface. The rate of movement away from the evaporating surface is diffusion controlled. Air movement is relatively nil close to the evaporating surface and the vaporized substance is transported from the surface through this stagnant air layer only by molecular diffusion. Since molecular diffusion coefficients of organic compounds in air are inversely proportional to the square root of molecular weight, the actual rate of mass transfer by molecular diffusion will be proportional to $P(M)^{-1/2}$. Thus, the vapour flux of a chemical from an inert surface can be described by $J = KP(M)^{1/2}$ (equation 1), J: vapour flux, P: vapour pressure, M: molecular weight and K: a proportionality constant. The magnitude of K depends on external conditions that control air exchange rates near the surface, such as the geometry, surface roughness and wind speed, etc.

Trifluralin vaporization rate and K value were calculated using equation 1. The vapour flux and K value were 1.292 $\mu\text{g}/\text{cm}^2/\text{h}$ and 292 (30°C , air flow rate of 0.48 litre/min and vapour pressure of 2.42×10^{-4} mm Hg). The vaporization rate under field conditions was much greater compared with the laboratory data because the air exchange rate is much greater in the field than in the laboratory (Spencer & Farmer, 1980).

The "wick effect" is another important mechanism providing movement of dissolved pesticide to the soil surface. When water evaporates from the soil surface, the resulting suction gradient causes appreciable water to move upwards to replace that evaporated, and the dissolved chemical will move upwards by mass flow in the water. The wick effect is magnified by the adsorption characteristics and water solubility of chemical and other factors affecting partitioning between the water, air and solid phases in the soil (Spencer & Farmer, 1980).

Pesticide volatilization from soil has been extensively studied. Transport upward through the soil to the soil-atmosphere interface occurs by either gaseous diffusion through the air-filled volume of the soil, or by the upward flow of soil solution induced by the water evaporation. In either case, the concentration in soil-air at the surface will be governed by soil water-air equilibrium, by Henry's Law, and such partitioning is a major determinant of the rate of pesticide volatilization from soil (Suntio et al., 1988).

There is in fact no enhancement of the volatility of a material due to the evaporation of water (codistillation), but reduction of soil moisture content increases the sites available for adsorption on soil particles and thus reduces volatility (Plimmer, 1976). In addition Upchurch (1966) reviewed and discussed codistillation with water as a mechanism to explain the substantial loss of some pesticides from soil surfaces. It is commonly and somewhat incorrectly stated that pesticide volatility has been enhanced by codistillation with water.

The minimum data needed to evaluate relative volatility in soil are vapour pressure and solubility of pesticide at various temperatures and desorption isotherms relating soil pesticide concentrations to either vapour densities or soil solution concentration. From the known relationship between vapour pressure, solubility, and temperature, an adsorption isotherm at one temperature would be adequate for predicting the vapour densities and soil solution concentrations at other temperatures (Spencer & Farmer, 1980). Consequently, no single physicochemical property can describe and predict the probable vapour behaviour and fate of a chemical in the environment or its likely method of transport in the atmosphere. However, relative vaporization rates are useful for environmental indices can be calculated from basic physical properties of vapour pressure, water solubility, adsorption and persistence, if reliable values are known for each of these properties at various temperatures (Spencer & Farmer, 1980).

There are a lot of studies to investigate the volatility of trifluralin under different conditions in different soil types. In the following the available studies will be reviewed. Kennedy and Talbert (1977) calculated that dinitroaniline herbicides undergo increasing losses when applied under field conditions and when incorporation is delayed. In addition, Savage and Barrentine (1969) evaluated the effect of incorporation depth of trifluralin in soil. Significantly more trifluralin was lost as a vapour at 40°C than at 30°C. Highly significant differences in trifluralin volatilization were detected with depths of incorporation depths. Maximum volatilization loss was from the surface application, less from shallow incorporation depth, and quite low vapour loss resulted from the deep incorporation treatment during a 6-week period. Horowitz et al. (1974) reviewed the reasons

explaining the importance of incorporation of trifluralin in soil is being apparently twofold; 1- the rapid dissipation from the soil surface due to photodecomposition and volatilization and 2- the very restricted movement in soil related to its strong adsorption and low water solubility.

Grover et al. (1988) measured the relative partitioning of triallate and trifluralin between the soil and air components following application and incorporation to a wheat field over the entire growing season. There were three distinct phases in the dissipation of the two herbicides in the soil; 1- an initial rapid dissipation phase, lasting about a week, with the vapour losses being the major route, especially under moist soil conditions; 2- a slow dissipation phase, lasting over the entire growing season, with volatilization, adsorption, and degradation as various routes of dissipation (75%) and no dissipation/breakdown phase following soil freezing in the fall; 3- thawing in the spring conditions typical of the Canadian prairies (about 20-25% carried over to the next growing season). Volatilization, which is dependent on the availability of soil water, was the dominant process for the dissipation and occurred continually until soil freezeup. Kearney and Konston (1976) found that volatilization is the major mechanism of loss of trifluralin from the soil. The loss was 6.44% during the first 3 weeks. In addition Harper et al. (1976) reviewed, the total seasonal volatilization loss was 25.9% of applied with 3.5% lost during application and 22.4% lost during the season. Spencer and Cliath (1974) reported that, the total loss by volatilization during the 48-day period was 2.45% of incorporated applied trifluralin to autoclaved Gila silt loam soil at the rate of 10 ug g^{-1} .

Parochetti et al. (1976) measured the vapour losses of eleven dinitroaniline herbicides from soil under controlled laboratory conditions for a 3-h period. No vapour losses of nitralin and oryzalin were detected at 50°C from moist Lakeland sand soil, whereas under the same conditions vapour losses approached 25% for benefin, profluralin and trifluralin.

As noted above volatility is a significant pathway for trifluralin dissipation from soil to the atmosphere. However this subject is very interesting from both the environmental fate point of view and with regard the analytical technique which concerns a lot of chemical including pesticides as air pollutants.

The reviewed studies indicate that the most effective factors, influencing volatility of trifluralin, are soil type, soil moisture content and temperature. Since trifluralin is widely used in the world under very variable conditions, a volatility study of trifluralin a major pathway of its dissipation from soil, the main medium in which trifluralin is used, under certain conditions is very important. No volatility study has been reported for trifluralin from an Iraqi soil in which trifluralin has been used widely as a preemerging herbicide mainly in cotton crop cultivation. Because of the specific climatic conditions experienced viz both hot and dry during the cotton growing season. three levels of moisture content (air dried, half field capacity, and field capacity) under two different temperatures (20 and 40°C) were chosen as experimental conditions. Scottish soil (Arkleston) which is much higher in organic matter than Iraqi soil and an acid washed sand were chosen to show the behaviour of trifluralin volatility in different soil types under the investigated conditions.

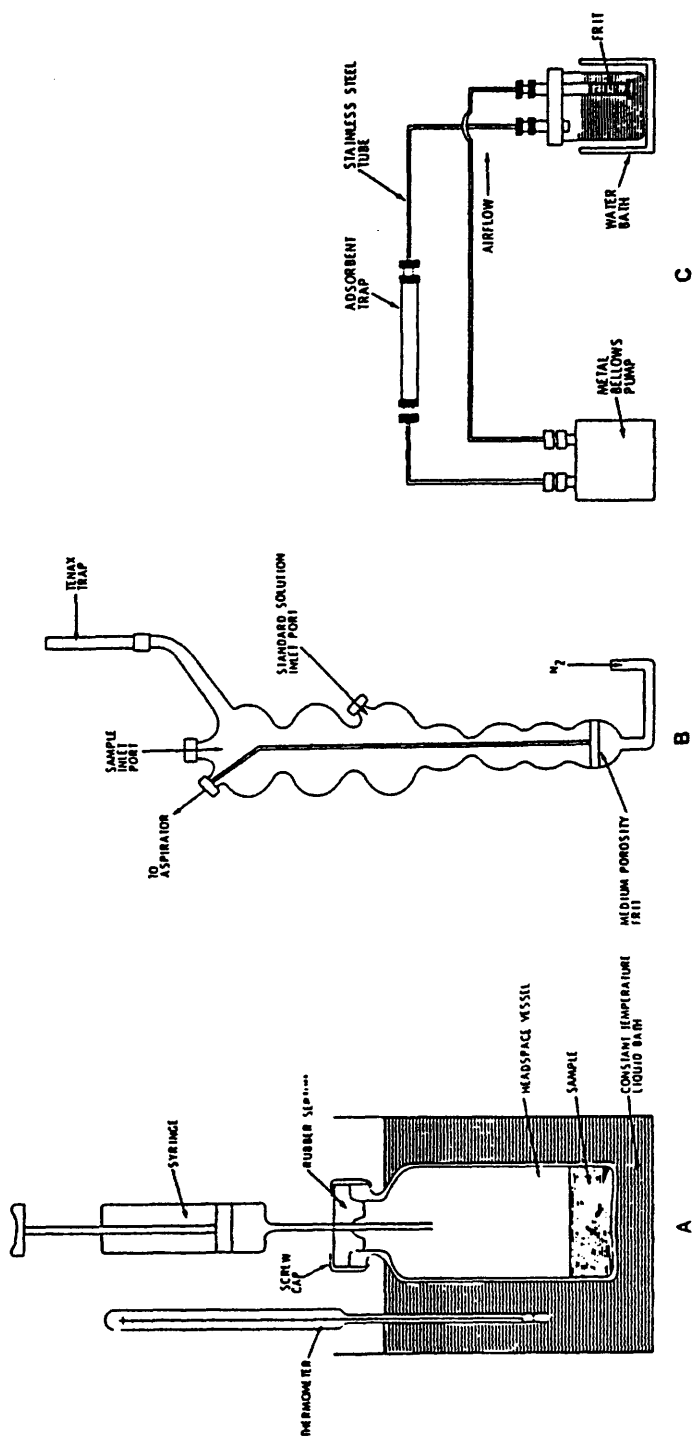
2.1.2 HEADSPACE ANALYTICAL TECHNIQUE

A- Headspace sampling

Sampling is obviously a key step in an analysis. The sampling of volatiles from the headspace has special requirements. In general the most important one, the low level of volatiles in headspace, needs a preconcentration of the volatiles to reach the detection limit, whereas the same technique could be used with small a volume sample of air from the headspace which contains high concentrations of volatiles.

There are two types of headspace sampling techniques (Fig.2.1). The first is a static headspace in which, the sample, either solid or liquid, is placed in a glass vial of appropriate size and closed with a rubber septum. The vial is carefully thermostated until equilibrium is established. The gas phase is sampled by syringe for manual procedures or with an electropneumatic dosing system in automated headspace analyzers. The second is a dynamic headspace and gas phase stripping in which, the substances which are low in concentration and have unfavourable partition coefficients can not be readily determined by static headspace method. The dynamic headspace method is a simple extension of the static headspace method. A continuous flow of gas is swept over and above the surface of a liquid, carrying the headspace volatiles to a trap where they are accumulated prior to analysis. The dynamic headspace or gas and vapour phase stripping techniques, combined with sorbent or cryogenic trapping are required to increase the

Figure 2.1 Apparatus used for gas chromatographic headspace analysis.
 A, static headspace sampling apparatus; B, gas phase stripping apparatus; C, closed-loop gas phase stripping apparatus.
 (Poole and Schuette, 1984).



amount of sample available for analysis (Poole & Schuette, 1984).

Van Dyk and Visweswariah (1974) reviewed and discussed the shortcomings and advantages of many sampling techniques for collecting pesticides in vapour-phase form such as adsorption, absorption, freeze-out and grab sampling. Many adsorbents were used in the adsorption technique for trapping pesticide vapours from air such as activated alumina, activated charcoal, potassium nitrate, Chromosorb 102, Chromosorb W, Chromosorb A, silica gel, and florosil. The collected amount of vapour-phase pesticide is dependent upon the total surface/mass of the adsorbent and the adsorbing capacity is also influenced by the natures of soil adsorbent and adsorbate, the geometric state of the adsorbent, the temperature, the velocity of the air stream, the concentration of the vapour-phase pesticide, and how far adsorption has proceeded. Most adsorbents are granular and supported in columns through which the air to be sampled is drawn.

Desorption may be achieved by heating and blowing air through the column or the column may be extracted with a suitable solvent.

In the absorption technique the trapping of vapours is based on solubility in the absorption liquid. Ethylene glycol, toluene, n-hexane, water, hexylene glycol, n-butyl alcohol, monoethanolamine, cholinesterase solution, 0.5N sodium hydroxide solution and 3% sodium bicarbonate solution-n-decane and cottonseed oil were used in the absorption technique. The absorption liquid must have a reasonably high solubility for the vapour phase pesticide and must be relatively non-volatile, noncorrosive, stable, nonviscous, nonfoaming, and preferably nonflammable.

The Freezeout technique is used to collect a sample desorbed from an adsorption column or to trap any vapour-phase pesticide that may have passed through other collectors without being collected. Dry ice trap and liquid nitrogen in an injection needle were used.

The Grab sampling technique is obtained with the use of an evacuated glass bottle or flasks or stainless-steel cylinders, the air sample is drawn through liquid absorbers to collect any material in vapour form.

Also reviewed are special sampling techniques such as continuous sampler-detection systems by various methods, enzymatic inhibition, bacterial luminescence, infrared, gas chromatography, nylon net coated with absorbent liquid, and paper strips treated with a chemical to collect and detect hazardous concentrations of some pesticides in air. In addition, the use of other solid and liquid traps has been reviewed by Haque and Freed (1975), Liquid absorption methods were applied to only one or a few chemicals, often at or near application sites where relatively high concentrations exist. Polyurethane foam is used as the trap. Liquid phases on solid supports are also used for trapping pesticide vapours, cotton seed oil on glass beads, glycerine on nylon nets, ethylene glycol on nylon nets, SE-30 on nylon nets, polyethylene on silica gel, 5% paraffin oil on Chromosorb A and bonded liquid phases, octadecylsilicone on Chromosorb.

A unique trap design permitting rapid cooling and heating for automated sampling and analysis of volatile organic compounds in air was tested. The method provides preconcentration and thermal desorption.

The collection and recovery efficiencies were 100q5% (McClenny et al. (1984)).

There are many studies employing various traps to sample the vapour phase of trifluralin. Bardsley et al. (1968) sampled the trifluralin vapours, above the trifluralin-soil closed system, using dried charcoal and calcium sulphate. Swann and Behrens (1972) used xylene as a trap for trapping trifluralin volatilized from soil, then the xylene solution was brought to a volume of 25 cm³ for analysis by ECD-GC. However, they found the technique they employed was not sufficiently sensitive to detect trifluralin vapour loss occurring more than 12 h after treatment. In another study, volatilized trifluralin was trapped in either hexane or ethylene glycol depending on the length of the measurement period (Spencer & Cliath, 1974). Trifluralin and its metabolites were trapped reasonably well from large volumes of air (120 m³) using 5% paraffin oil on Chromosorb A in the high volume sampler. The ethylene glycol trap also used as trifluralin vapour trap by pulling the air by vacuum through the trap (Harper et al., 1976). A column containing 12 g Florisil was used to capture the vapours of eleven dinitroaniline herbicides. The recovery was 91.4% upon elution of Florisil columns with 35 cm³ acetone (Parachotti et al., 1976). Kearney and Konston (1976) used a polyurethane plug placed into a filter funnel to trap the vapours of butralin and trifluralin arising from soil surfaces. The plugs were then analysed periodically for 4 weeks by Soxhlet extraction for 2 h with benzene-acetone (1:1) v/v. More recently, Grover et al. (1988) used polyurethane foam plugs (45 cm dia. by 50cm long) with 25 L min⁻¹ flow rate to trap trifluralin vapours throughout a growing season. The traps were Soxhlet extracted with 300 cm³ of n-hexane for 2 h and the extracts passed through a Fl-

orisil column for clean-up and analysed by gas chromatography. Trifluralin was sampled using a cartridge consisting of 4 mm * 8 cm thin walled stainless steel containing 0.1 g of 4% OV-101 on 100/120 mesh Gas Chrom. Q followed by a thermal desorption technique to quantify trifluralin vapours (Mongar & Miller, 1988). Wallace et al. (1988) evaluated the efficiency of an activated charcoal and polyurethane foam trap. It retained 93-100% of eight pesticides including trifluralin.

A comparison was conducted by Ligocki and Pankow (1985) between two methods for collection of ambient organic vapours in field sampling. The two methods were adsorption/solvent extraction with polyurethane foam plugs and adsorption/thermal desorption with Tenax-GC cartridges. The results indicated the first method is best suited for the collection of nonvolatile compounds, using high sample flow rates and the second method is a versatile method which is well suited to sampling volatile compounds either with very low flow rates or with higher flow rates to obtain greater time resolution.

Tenax-GC is a recently introduced porous polymeric material based on 2,6-diphenyl-p-phenylene oxide, originally developed as a GCS column packing. It is hydrophobic and is excellent for adsorbing volatiles from the atmosphere at room temperature (Braithwaite & Smith, 1985). Billings and Bidleman (1980) used Tenax for trapping hydrocarbon pesticides.

Many literature reports indicate that Tenax is the best adsorbent for trapping organic compounds covering a wide range of molecular weights. Mieure and Dietrich (1973) found three packed short columns sa-

tisfactory for trapping many organic chemicals from air and water. The backing materials are Chromosorb 101, Chromosorb 105 and Tenax-GC. The trapped components were eluted into the analytical column thermally. The polymeric beads, Tenax-GC, Porapak Q, Chromosorb 101, and Chromosorb 104 are >90% efficient in trapping vapours of many organic compounds including nitroso and nitro compounds from air. In addition liquids such as Carbowax 600 and 400 and oxypropionitrile coated or chemically bonded to supports were also highly efficient (>90%) (Pellizzari et al., 1975a). They also reported many factors influencing sorbent performance such as flow rate, air temperature, humidity, surface area, particle size, porosity, solute capacity, sorption mechanism and degree of solute affinity. Boyd (1984) reviewed many uses for Tenax-GC, in environmental, food and medical research to trap and concentrate traces of organic compounds from dilute media. He used Tenax-GC for trapping potato volatiles and the potato sprout suppressants, chloropropham and tecnazene. Atlas et al. (1985) evaluated the collection efficiency of Tenax (0.6 g) and charcoal (1.5 g) traps, Tenax has excellent trapping characteristic for C₉-C₁₉ hydro-carbon compounds and the retention efficiency of more volatile compounds improved with smaller air sample volumes. The charcoal traps used to reconcentrate the compounds desorbed from Tenax also worked well. Otson et al. (1987) used a sorbent tube containing Tenax followed by a tube containing XAD-2 resin to trap 15 airborne polycyclic aromatic hydrocarbons. They used glass tubes containing 100 mg front and 50 mg backup sections of Tenax or 150 and 75 mg sections of XAD-2 resin respectively. The combined flow rate for nitrogen and air through the sampling train was 2 L min⁻¹. The sorbents were extracted by cyclohexane for analysis.

The parameter which characterizes the collection efficiency of a particular sorbent for a particular analyte is the breakthrough volume (the volume of gas, containing analyte, that can be passed through the sorbent bed until its concentration at the outlet reaches some fraction of its inlet concentration). Several methods have been used to measure the breakthrough volume of sorbent traps. These include purging a trap directly into a flame ionization detector, field sampling with dual traps in series, loading traps with a known amount of analyte which is then purged with a volume of gas and the amount of sample remaining determined, or by estimation from the measurement of chromatographic retention volume data at different temperatures (Poole & Schuetz, 1984).

Van Dyk & Visweswariah (1974) reviewed many studies using a range of flow rates during sampling of air for pesticide determinations. The range was $0.0008-0.018 \text{ m}^3 \text{ min}^{-1}$.

Analysis of a second charcoal trap placed in series downstream of the primary trap was indistinguishable from a blank trap (Atlas et al., 1985). When backup adsorbent traps are utilised, the amount of material found on the backup trap provides an indication of the efficiency of the trapping process. Breakthrough of an analyte on an adsorbent is a function of the ambient temperature, the sample volume, the adsorbent volume, the affinity of the analyte for the adsorbent, and the dimensions of the adsorbent trap. The temperature effect on breakthrough can be large, due to the strong dependence of vapour pressure on temperature (Ligocki & Pankow, 1985).

B- Headspace analysis

The methods for the transfer of volatile compounds from a porous polymer adsorbent trap onto a GC column are documented by many researchers. There are two techniques used-solvent elution or thermal desorption.

The solvent elution has been used for extraction of pesticides or other compounds from the adsorbent trap, then the eluant concentrated to a small volume and injected into the GC column (Van Dyk & Visweswariah, 1974; Haque & Freed, 1975; Onuska & Karasek, 1984; Otson et al., 1987). Traps containing Tenax and XAD-4 resin or Tenax AT alone to collect several fumigants from purged grain and table ready food are eluted with hexane for detection (Heikes, 1985; Heikes & Hopper, 1986; Heikes, 1987).

Ligocki and Pankow (1985) tested two methods for the collection of ambient organic vapours at the ng m^{-3} to ug m^{-3} level in field samples. The methods were adsorption/solvent extraction with polyurethane foam plugs and adsorption/thermal desorption with Tenax-GC cartridges. They found that, Tenax-GC was a versatile method which was well suited to sampling with very low flow rates or with higher flow rates to obtain greater time resolution for high to intermediate volatility organics. Atlas et al. (1985) used a different thermal technique using the combined heat/solvent microextraction system for trapping organic compounds. Compounds sorbed on Tenax are backflushed into a charcoal trap, then the charcoal is rinsed three times with a total of 12-15 μL of solvent, each rinse being carefully withdrawn from the trap by syringe and transferred to a capillary tube. The sensitivity

of the analysis is ~~is~~ 50 times better than the normal solvent desorption technique and it is only a factor of 5-6 less sensitive than heat desorption alone.

An advantage of the thermal desorption method is that all of components from the headspace sample that have been adsorbed on a column trap are transferred onto a GC column. This is in contrast to an extraction procedure in which the volume of extracted sample is reduced to a certain known volume and an aliquot of about 1:1000 used for analysis. Thus, by using thermal desorption, a gain of a factor of 1000 in sensitivity may be achieved. Another advantage of the thermal desorption method is that volatile components are not lost during the extraction and preconcentration steps (Onuska & Karasek, 1984). In addition Coutant et al. (1985) discussed the mechanics of sampling with reversible adsorption, when presented with a simple model for calculating sampling rates and employed Tenax-GC as the sorbent for sampling 17 volatile organic compounds. They also reported several advantages for the thermal reversible adsorption which is particularly well suited to low level sampling and analysis of volatile compounds. These advantages include independence from solvent contamination, increased sensitivity because of the availability of the whole sample for analysis, and more rapid sample turnaround. An obvious disadvantage of this technique is that you can only get one run per treatment.

Several workers have used a thermal desorption technique. The thermal desorption was used to flush the volatiles from the porous adsorbent trap into the GC column without dilution (Pellizzari et al., 1975b; Boyd, 1984; Onuska & Karasek, 1984; Braithwaite & Smith, 1985; Greaves et al., 1985; Ligocki & Pankow, 1985).

The adsorption/thermal desorption preconcentration technique, using Tenax-GC as a trap, was used for trapping polycyclic aromatic hydrocarbons and pesticides such as Gamma-BHC, heptachlor, dieldrin, and DDT (Pankow & Kristensen, 1983). Thermal desorption of the pharmaceuticals was performed, using a Tenax trap (Wampler et al., 1985).

The desorption temperature and time required to strip the sample from the sorbent depended on the properties of the sample, but temperatures of 250 - 350°C and times from 5 to 30 min are common at 15 cm³ min⁻¹ and temperature of 270°C for 8 min is sufficient to recover most of the organic compounds trapped from air. Passing carrier gas through the heated trap rapidly flushes the sample onto the analytical column. The desorption process can be performed manually or can be automated (Poole & Schuette, 1984).

Tenax was chosen in this study, in an attempt to develop an analytical method for trifluralin vapours in the headspace of trifluralin treated soils. This choice was due to: 1- The ability of Tenax to trap organic compounds of a wide range of molecular weights. 2- Pre-concentration of the volatiles at room temperature. 3- The stability of the Tenax at high temperature enables the Tenax to be used in the thermal desorption technique. The characteristics 2 and 3 provide a highly sensitive analytical method which may be necessary under certain conditions when the expected volatility of trifluralin is low.

2.2 EXPERIMENTAL

The experimental section involves a system designed to be suitable for the study of the volatility of trifluralin from soil under various dynamic conditions and utilizing a porous polymer adsorbent (Tenax) trap to trap and preconcentrate the trifluralin vapours. This section also involves the development of a thermal desorption technique to provide a sensitive analytical method sufficient to detect trifluralin vapours in the treated soil headspace. In addition, this section contains other related integrated aspects.

2.2.1 Chemicals

Trifluralin 99% was purchased from Alltech Associates/Applied Science (U.K.).

Tenax TA 80-100 mesh was purchased from Jones Chromatography MidGlamorgan, U.K.

The quality of all organic solvents used in this work was analytical reagent grade except n-hexane which was glass distilled; acetone, dichloromethane, and methanol were purchased from May & Baker Ltd, England and n-hexane from Rathburn Chemicals Ltd, Scotland.

Hydrochloric acid and sodium sulphate anhydrous were analytical reagent grade (BDH Chemicals Ltd, England).

Activated carbon was purchased from Norit, Netherlands.

2.2.2 Soil-air flow model system construction

The system was constructed from a pressurised air cylinder (B.O.C. Glasgow Ltd) which was fitted with a pressure regulator (C.S. Milne Ltd, Glasgow). The air was allowed to flow through activated charcoal (Norit N.V., Amersfoort, Netherlands) in a gas purifier with an internal volume of 200 cm^3 connected through a water bottle containing distilled water to obtain clean and humid air. The air flow rate was adjusted, using a fine flow rate adjustment (Porter Instrument Company, Hatfield, PA, USA) which was connected with a glass manifold (5mm, internal diameter) to distribute the air among the vessels containing treated soil. The air was used to sweep the trifluralin vapours from the headspace over the treated soil onto the Tenax trap. The air flow rate was measured, using a soap bubble flow meter from the end of the Tenax trap. It was set at $10\text{--}12\text{ cm}^3\text{ min}^{-1}$. The vessel which was used to contain the treated soil was constructed from a modified reaction vessel. The vessel was 80 mm in depth and with 100 mm internal diameter. Two glass tubes were attached at 50 mm from the bottom of the vessel for passage of the air in and out of the vessel. The first tube, with 10 mm outer diameter was connected to the Tenax trap by a PTFE tube 30 mm internal diameter. The vessel was fitted with a removable head which was also modified from a reaction vessel, 40 mm in depth and with 100 mm internal diameter. The two parts were sealed by using a PTFE ring, 110 mm outer diameter, 0.5 mm thick and metal clips to form a headspace volume of 549.8 cm^3 over the treated soil (Fig.2.2 and Plate 2.1). All the connections were made of copper, glass and PTFE to avoid any interference. The vessels and

Tenax trap were covered with aluminium foil to avoid any photolysis of trifluralin by U.V. The vessels were put in a water bath at a suitable depth to maintain the treatments at a particular temperature.

Fig.2.2 Schematic diagram of the soil-air flow system for studying trifluralin volatilization from soil. 1-Air cylinder. 2-Pressure regulator. 3-Activated charcoal. 4-Air humidifier. 5-Fine flow rate adjustment. 6-Manifold. 7-soil headspace. 8-Treated soil. 9-Water bath. 10-Tenax-trap.

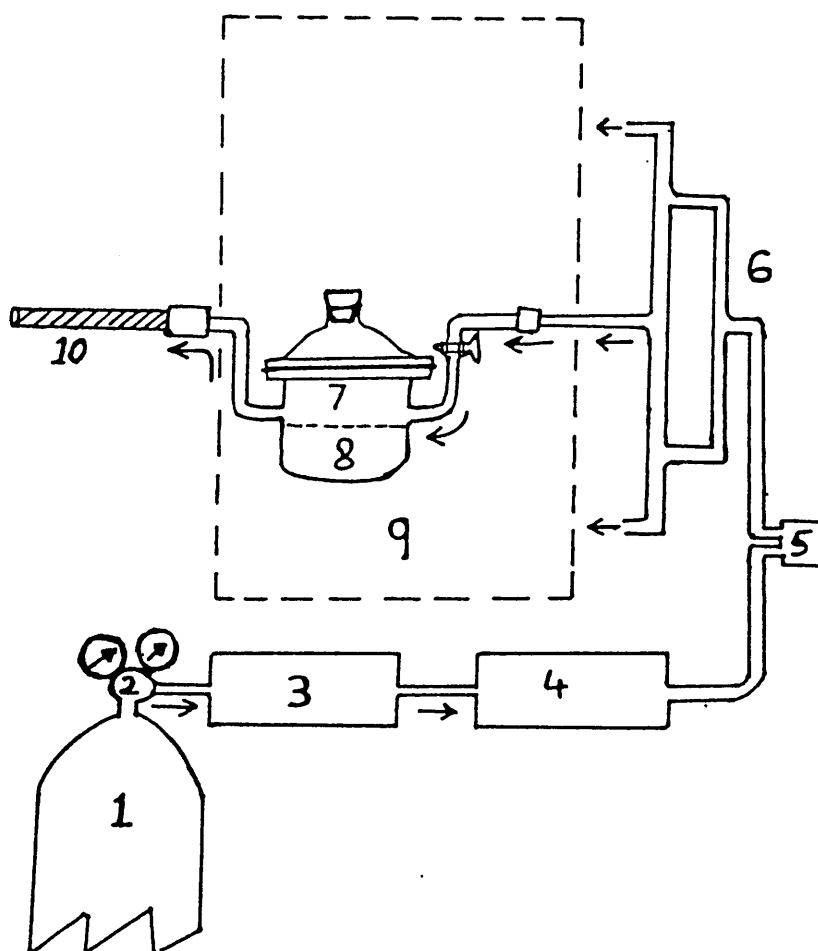
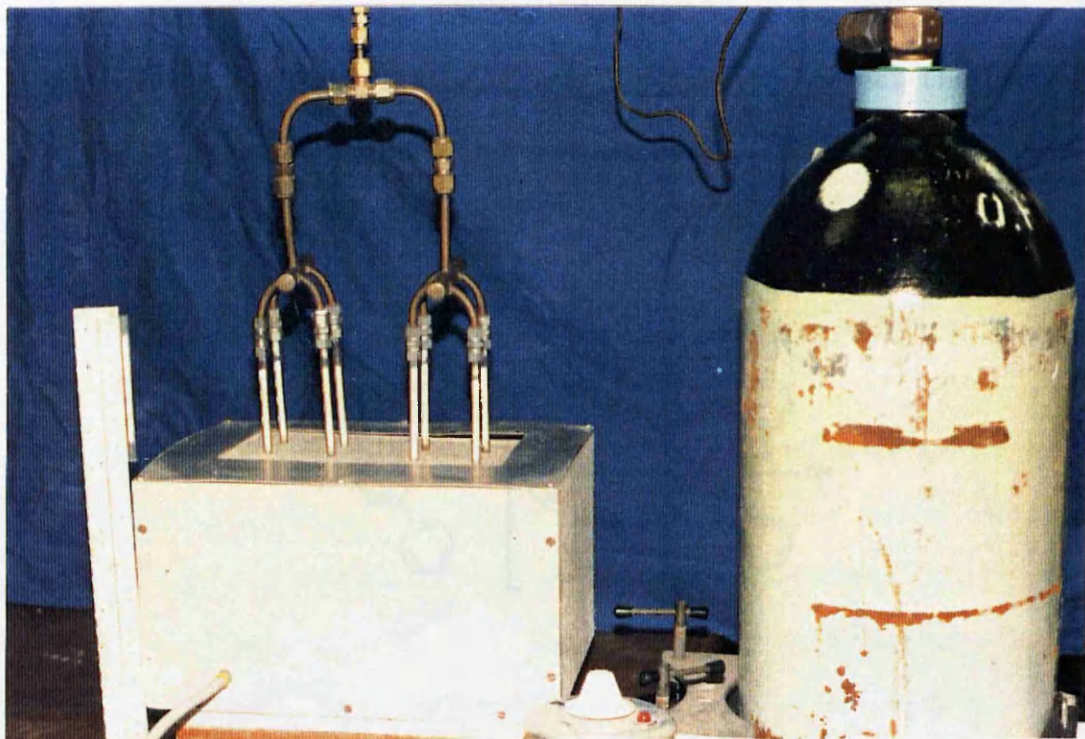


Plate 2.1 The vessel which contains a treated soil, as a part of the soil-air flow system for studying trifluralin volatilization.



Plate 2.2 The heating block for Tenax-trap conditioning and purification.

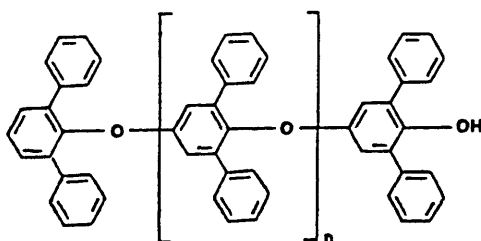


2.2.3 Tenax and Tenax trap preparation

A- Tenax

Tenax is a porous polymer based on 2,6-diphenyl-p-phenylene oxide. Tenax is used rather than a volatile trap for the extraction of organic microcarbons in water containing pesticides, polycyclic aromatic hydrocarbons, and atmospheric pollutants. The extraction of pesticides from surface waters by adsorption on Tenax yields results equivalent to those obtained by the liquid-liquid extraction procedure when applied to drinking and surface waters (Onuska & Karasek, 1984).

Tenax-GC is a relatively new porous polymer packing material and is suitable for the separation of high boiling polar compounds such as alcohols, polyethylene glycols, diols, phenols, mono and diamines, ethanolamines, amides, aldehydes and ketones. A rather unusual application of Tenax-GC was for experimental molecular analysis of the Martian Soil by the Viking, Mars Lander to detect the presence of organic compounds and thus provide evidence for the existence of life forms (Braithwaite & Smith, 1985).



Tenax

The polymer Tenax has a molecular weight of $5 \cdot 10^5$ to 10^6 and a

surface area of $19 - 30 \text{ m}^2 \text{ g}^{-1}$. Tenax adsorbs a wide range of organic compounds. However, compounds of molecular weight lower than about C_7 are not quantitatively retained at room temperature. Tenax has a low efficiency for the retention of water and is thermally stable, permitting the use of high desorption temperatures. Tenax-GC is unique in terms of its thermal stability. It may be used isothermally at temperatures up to 375°C and in temperature programmed separations it has been used at temperatures in excess of 400°C .

The Tenax sorbent may require decontamination before use by Soxhlet extraction overnight with pentane and then methanol, followed by thermal conditioning of the dried sorbent in a stream of purified helium at $250\text{--}350^\circ\text{C}$ for 24 h.

Excess water, however, may cause sample loss in the desorption step due to microfog formation and/or blockage of the precolumn. Passing a dry stream of gas through the cartridge for a short time or storing it in a sealed container with desiccant will usually eliminate these problems (Poole & Schuette, 1984).

B- Tenax ability to trap trifluralin vapours

Headspace vapours of the crystals of trifluralin were withdrawn from a 250 cm^3 sealed bottle through a Tenax trap by a 50 cm^3 syringe. The bottle was placed in a 40°C water bath to enhance trifluralin volatility. The trap was connected between the syringe plunger and the needle which was inserted into the Teflon lid of the bottle.

The other parameter which characterizes the collection efficiency of Tenax for trifluralin vapours is the breakthrough volume. The highest expected headspace concentration was used for this test. The test was carried out by sampling the headspace using dual Tenax traps in series, then the two traps were analyzed to test the breakthrough of trifluralin.

C- Tenax trap preparation

The Tenax trap was prepared according to the procedures of Boyd (1984) and Atlas et al. (1985).

1- A 100 mm length of borosilicate glass tube with 6.5 mm outer diameter was placed in concentrated hydrochloric acid (AR, BDH Ltd, Poole, England) for 24 h, then thoroughly rinsed with deionised water followed by acetone (AR, BDH, Ltd, Poole, England) and heated in an oven at 220°C for 2 h.

2- The tube was packed with 100 mg of Tenax AT 80-100 mesh (Jones Chromatography, England) which was held in place by plugs of silanised glass wool.

3- The Tenax trap was conditioned, purified by heating under a N₂ gas (B.O.C. Glasgow Ltd) of flow 20-30 cm³ min⁻¹ at 280-300°C for 2 h, using a heated block.

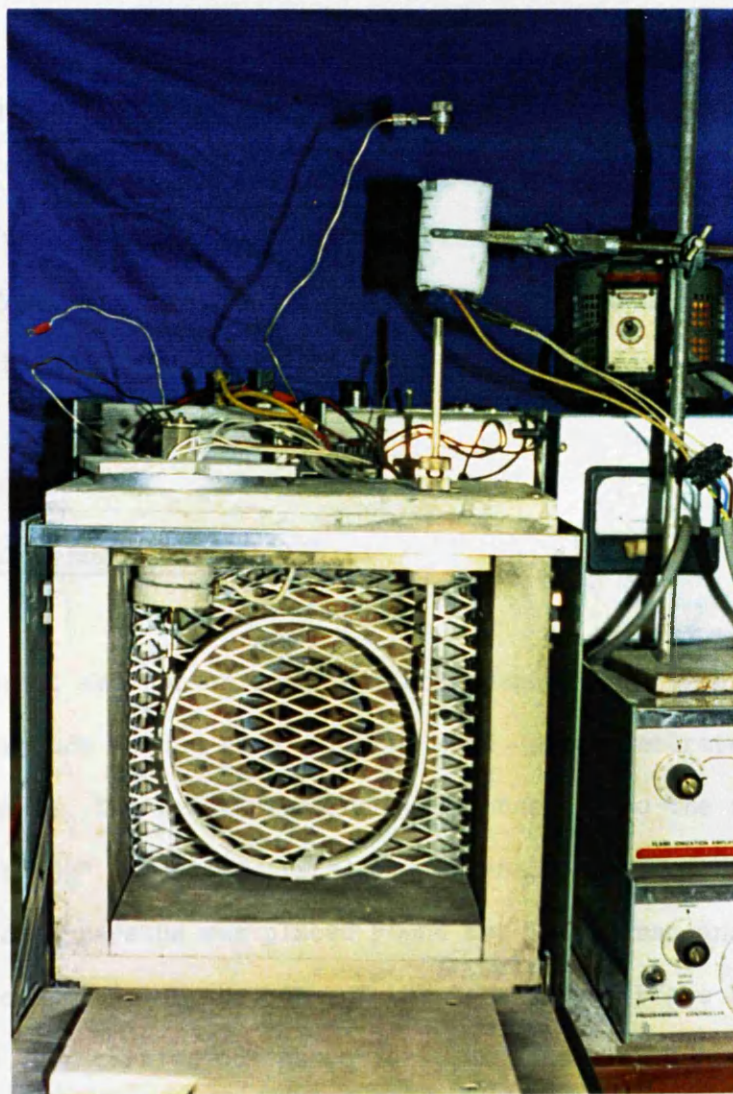
The heated block (Plate 2.2) was constructed from a block of aluminium 200 mm long, 7.5 mm deep and 100 mm wide. It was drilled to

take six 150 W cartridge heaters (Hedin Ltd). The block was drilled with eight equally spaced 7 mm diameter holes into which the Tenax traps were inserted. The whole block was surrounded with 10 mm mar-anite heat insulation and placed in an asbestos lined box (19.5 * 29.5 * 16.5 cm) and surrounded by sand to provide further thermal insulation. A manifold tube was constructed from $\frac{1}{4}$ " outer diameter copper tubing (Alltech Associates) to enable eight Tenax traps to be purged with N₂ during conditioning and purifying of the Tenax traps. The Tenax traps were connected to the manifold with $\frac{1}{2}$ " couplings (Dralim, Phase Separations Ltd). The traps were purged with N₂ at 20-30 cm³ min⁻¹ for 1 min then inserted into the block and heated for 2 h. The traps were then removed and allowed to cool to room temperature under a N₂ gas flow. The traps were then disconnected and sealed with PTFE caps 30 mm in length and 10 mm outer diameter drilled to a depth of 20 mm with a 6 mm drill. The traps were stored till used. This method was used throughout the work and step 3 was repeated as necessary before sampling.

2.2.4 Analysis of Tenax-trap

A- Headspace sampling

Trifluoromethane vapours were sampled from the headspace of treated soil (549). Plate 2.3 Connection of Tenax-trap to GC column in the thermal desorption technique.



2.2.4 Analysis of Tenax trap

A- Headspace sampling

Trifluralin vapours were sampled from the headspace of treated soil (549.8 cm^3) every 24 h for a 13-day period, using a Tenax trap at an air flow of $10\text{--}12 \text{ cm}^3 \text{ min}^{-1}$. The sample volume was 15.84 L which changed the headspace above the treated soil, 28.81 times every 24 h.

The Tenax trap was sealed by PTFE caps immediately after sampling and the Tenax trap was analyzed within 2 h with the exception on the occasion when some samples were stored in a fridge mostly for up to 2 days before analysis. The Tenax traps were stored in sealed polyethylene bags.

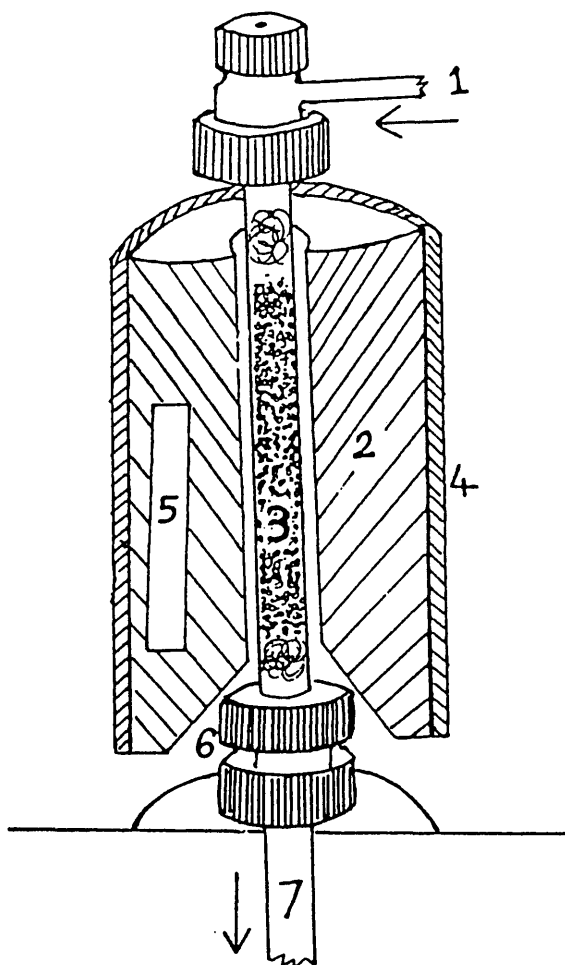
B- Thermal desorption technique

The thermal desorption technique was adapted for the analysis of trifluralin vapours which were trapped and preconcentrated on the Tenax precolumns. The Tenax precolumn was connected to the top of the GC column with a $\frac{1}{4}$ " coupling (Dralim, Phase Separations Ltd) then a heat desorption apparatus was placed round the Tenax trap and the carrier gas was connected to the top of the Tenax trap (Plate 2.3). All manipulations were carried out as quickly as possible, preferably within a few seconds to minimise the interruption of the carrier gas flow to the GC column. To avoid cold spots in the system, the bottom metal connector was placed in thermal contact with the heat desorption apparatus.

C- Heat desorption apparatus

A heat desorption apparatus was constructed from a block of aluminium, 30 mm in diameter and 70 mm long. The centre of the block was drilled with a 7 mm diameter hole. The block was heated by a 150 W cartridge heater (Hedin Ltd) which was inserted into the block. The outer surface of the desorption block was covered with glass wool and PTFE sheet which served as a thermal insulator (Fig.2.3). The block was maintained at 240°C.

Fig.2.3 Heat desorption apparatus: 1-Carrier gas inlet; 2-Aluminium block; 3-Tenax-trap; 4-Insulation; 5-Cartridge heater; 6-, " coupling; 7-GC column.

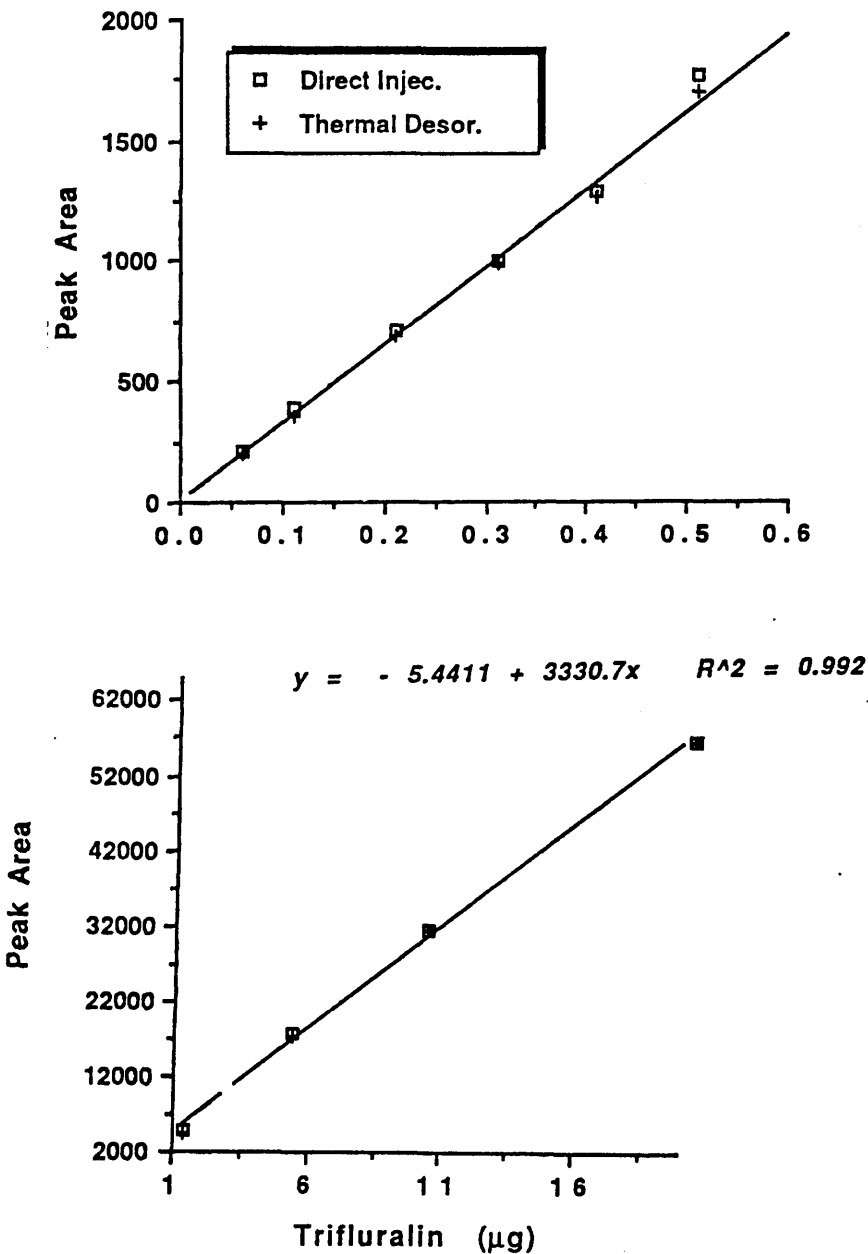


D- Gas Chromatography

A Pye 104 (Pye Unicam Ltd) Gas Chromatography, equipped with flame ionization (F.I.D.) detector with a silanised glass column (1.66 m, 5 mm) packed with a mixture of 1.5% OV-17 and 1.95% OV-202 on Chromosorb W-HP 100/120 mesh (Alltech Associate), was adopted for this work after testing its ability to give a good separation of trifluralin. Trifluralin was eluted in less than 7 min. The carrier gas was nitrogen (B.O.C. Glasgow Ltd) at $30 \text{ cm}^3 \text{ min}^{-1}$. The oven and detector temperatures were 165 and 250°C respectively. Detector gasses, air and H_2 (B.O.C. Glasgow Ltd) were at 120 and $30 \text{ cm}^3 \text{ min}^{-1}$ respectively. All calculation such as, calibration and integration were achieved using a Spectro-physics, Sp 4290 integrator. Comparison of the linear response of the flame ionization detector to trifluralin, using the direct injection and thermal desorption techniques is shown in Fig.2.4.

The entire procedure, from sample collection to chromatographic analysis, can be performed in less than 30 min.

Fig.2.4 Comparison of the linear response of flame ionization detector (F.I.D.) to trifluralin, using the direct injection and thermal desorption techniques.



E- Retention time, linearity, and trifluralin recovery from Tenax trap assessments

An assessment was carried out to measure linearity of the thermal desorption of trifluralin from the Tenax traps and its retention time. A series of trifluralin standard solutions were made up in glass distilled n-hexane, 10, 20, 40, 60, 80, 100, 200, 1000, 2000, and 4000 $\mu\text{g cm}^{-3}$. All of these were kept in stoppered volumetric flasks in a fridge when not in use. 5 mm^3 from each solution was injected onto the middle of a Tenax trap, using a 10 mm^3 syringe (Hamilton, series 700, Switzerland) then the Tenax traps were analysed after 30 min of equilibration as described in Section B. The same volume, 5 mm^3 , from the same standard solutions was injected directly onto the GC column to compare the retention time and linearity of both the thermal desorption and direct injection techniques. Each treatment was replicated five times.

The recovery of trifluralin from the Tenax trap was calculated as a percentage of the peak areas from the five replicates based on the mean of the five replicates from the direct injection. The mean of the five replicates at each level was used as a correction factor, using the nearest recovery value as the correcting factor for the daily detected amount.

F- Effect of storage period on the recovery of trifluralin from Tenax trap under different conditions

Fifteen freshly prepared Tenax traps were injected with 100 μg

cm³ trifluralin in n-hexane in the middle of the trap, using a 1 mm³ syringe (Hamilton, series 7001, Switzerland). The traps were sealed with PTFE caps. Five of them were analysed after 1 h of equilibration and the remaining ten were stored in the fridge (5°C) in sealed polyethylene bag. After storage for five days five of them were analysed and the remaining five were analysed 10 days later. To test the effect of temperature, the same procedure was followed except the traps were stored at room temperature (20°C ± 2).

2.2.5 Soils and soil treatment

Arkleston sandy loam, Iraqi clay loam and acid washed sand were used in the trifluralin volatility study from soil. Soil samples were collected from 15 cm depth from five random sites of each soil, using an auger. The soil samples were mixed and allowed to reach an air dried condition then they were screened through a 2 mm mesh sieve. The physical and chemical properties of the soils were analysed according to Khan (1987).

The water field capacities were determined using the following procedure. 100 g oven dried and sieved soil (2 mm mesh) were held in a plugged funnel using a wet cotton wool plug. The soil was flooded with 100 cm³ distilled water then the funnel sealed with a watch glass and left to equilibrate overnight. The moisture held by the 100 g oven dried soil was determined on an oven dry basis as a percentage. The soils characteristics are presented in Table 2.1.

The procedure for treating the soil was as follows, soil autoc-

laved for 1 h at 120°C and 15 Lb in⁻¹. This was carried out twice at 3-day intervals to prevent any microbial degradation of the trifluralin in this procedure.

A 1000 ug cm⁻³ trifluralin standard solution was made up in glass-distilled n-hexane in a stoppered volumetric flask. 3 cm³ of the standard solution were added to 300 g soil (dry weight) at air-dried condition in a 750 cm³ glass jar. The addition of 3 cm³ was in three portions and the treated soil was mixed thoroughly after each addition. Uniform distribution of trifluralin throughout the soil was assured by mixing with a glass rod and shaking the jar for 30 min, using an end-over-end shaker. Distilled water was added to the treated soil to bring it to $\frac{1}{2}$ field capacity or to field capacity. The treated soil was placed in the vessel which will be describe later. The Tenax trap was connected immediately after sealing the vessel. The Arklestone soil treatment was carried out in three replicates while the other treatments were unreplicated. An appropriate control treatment was included. The soil treatment level was detected by analysing three samples at zero time. All the vessel and the Tenax traps were covered with aluminium foil to avoid the light. The vessel were placed in a water bath at the same level as the treated soil surface to obtain the desired temperatures (20°C and 40°C).

Table 2.1 Soils characteristics

	IRAQI soil	ARKLESTON soil
Coarse sand	11.6%	32.7%
Fine sand	8.9%	35.3%
Silt	28.1%	16.3%
Clay	48.3%	15.7%
Organic matter	2.8%	7.5%
pH in water	7.7	5.6
Air dried	5.6%	3.7%
moisture content		
Field capacity	49.9%	31.6%
moisture content		
Textural class	Clay loam	Sandy loam

2.2.6 Recovery of trifluralin from soil

100 ug of trifluralin in 1 cm³ were added to 10 g of air dried soil in Teflon bottles. The treatment was replicated three times. The same procedure which will be mentioned in section (2.2.7) was used for the extraction of trifluralin from soil. The extracts were analysed as in section (2.2.7).

2.2.7 Analysis of trifluralin residues in soil

There are many methods for the extraction and detection trifluralin residues from soil.

Various solvent systems are used to extract trifluralin from soil such as methanol (Probst et al., 1967; Harrison & Anderson, 1970; Smith, 1981), a mixture of benzene-2-propanol (2:1) (Soderquist et al., 1975), 10% aqueous acetonitrile (Smith, 1981; Moyer & Elder, 1984), n-hexane (Savage & Barrentine, 1967), and n-hexane-acetone (3:1) (Savage & Jordan, 1980).

Also different detection methods have been used to quantify trifluralin residues such as the colorimetric method of Holzer et al., (1963) an integrated method involving gas chromatographic and colorimetric techniques (Payue et al., 1974), gas chromatographic methods using an electron capture detector with various packing columns (Savage & Barrentine, 1969; Savage & Jordan, 1980; Smith, 1981), a gas chromatographic method using thermal conductivity detector (Leitis & Crosby, 1974), a gas liquid chromatography/mass spectrometry procedure to simultaneous determine trifluralin and benfin (Downer et al., 1976), and also a radioactive procedure (Smith & Muir, 1984).

The procedure used here for extraction and detection was developed in this work to accommodate available supplies and equipment.

10 g soil sample (oven dry basis) plus 50 cm³ n-hexane -acetone (3:1) were placed in a 200 cm³ Teflon bottle. The bottle was shaken, using an orbital shaker for 1 h. The suspension was centrifuged in

the same bottle at 4500 R.P.M. for 10 min (Mistral 2000 centrifuge, Fisons plc, England). 25 cm³ of supernatant were transferred to a 50 cm³ round bottom flask, using a 25 cm³ pipette. The aliquit was passed through anhydrous sodium sulphate. The filtrate was evaporated to dryness, under vacuum using rotary evaporator (Buchi) at 35°C. The residues were collected in n-hexane for analysis, using a gas chromatograph equipped with a flame ionization detector using the same conditions mentioned in Section (2.2.4-D). Trifluralin residues were quantified by integrating the injected amount of the sample with two standard solutions using the Sp 4290 spectro-physics integrator.

2.2.8 Adsorption of trifluralin on soil

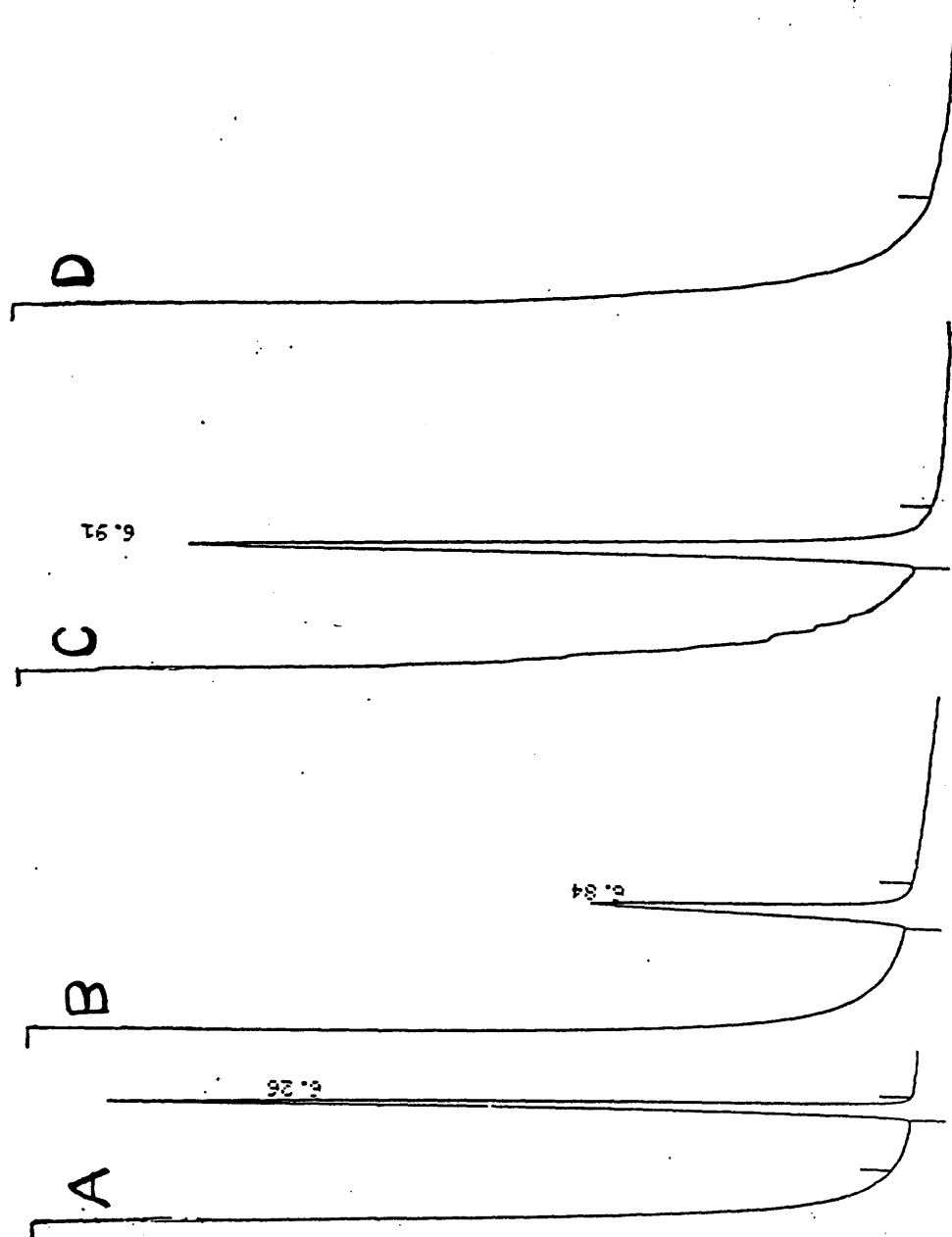
Trifluralin was dissolved in n-hexane to prepare a stock solution then three levels of trifluralin were made up (30, 50, and 70 ug cm⁻³). Aliquots of 1 cm³ from each level were added to a 250 cm³ flask, then 100 cm³ of distilled water were added to each flask after evaporating off the hexane using a stream of nitrogen gas yielding different aqueous solutions (0.3, 0.5, and 0.7 ug cm⁻³). This range of levels was used to avoid the saturated state (solubility of trifluralin in water is 0.5 - < 1 ug cm⁻³).

Triplicate 1 g samples of each soil or acid washed sand based on dry weight, were added. The flasks were sealed with Quickfit stoppers and incubated for 24 h on an orbital shaker (Gallenkamp, England) at 20°C ± 2. Triplicate control treatments without soil were treated in the same manner and used as standards. After the equilibration period, the contents of the flasks were transferred into 250 cm³ centrif-

uge Teflon bottles and the bottles were sealed and centrifuged at 4500 R.P.M. for 10 min. Aliquots of 50 cm³ of supernatant were extracted three times by partitioning with 25 cm³ of dichloromethane. The combined extractants were evaporated under vacuum using a rotary evaporator at 35°C till dryness. The residues of trifluralin were collected in 2 cm³ n-hexane and detected by gas chromatography as mentioned in Section (2.2.7).

Fig.2.6 Typical chromatograms of (A) 0.3 ug trifluralin injected directly to GC column; (B) 0.5 ug trifluralin injected into the Tenax-trap and desorped thermatically onto GC column; (C) and

(D) Headspace samples of Arkleston soil at Half field capacity and 40°C for treated and blank treatment respectively.



2.3 RESULTS AND DISCUSSION

A- Headspace analysis

Many experiments were carried out to assess the efficiency of sampling of trifluralin in the headspace by using the Tenax absorbent trap and thermal desorption. The assessments were as follows:

1- The ability of Tenax absorbent to trap trifluralin vapours. Because no available literature for using Tenax for trapping trifluralin vapours was available, an assessment was necessary in the beginning of this work. Tenax displayed an excellent ability to trap trifluralin vapours when the headspace of trifluralin crystals in sealed bottles was withdrawn through the Tenax trap, using a syringe. In addition, the breakthrough of trifluralin vapours was tested by connecting two Tenax trap units in series. The trapped vapours were found just in the first trap which faced the headspace.

2- The results of retention times for trifluralin when desorbed from the Tenax trap onto the G.C. column, using the thermal desorption technique and also when injected directly into the G.C. column are shown in Table 2.2. The difference in the mean of five replicates of six trifluralin levels was 0.52 min more in the case of the thermal desorption technique. In other words the trapped trifluralin remains 0.52 min more in the system in the thermal desorption technique compared with the direct injection of trifluralin ($6.74 \text{ min} \pm 0.19$ for thermal desorption technique and 6.22 ± 0.03 for direct injection).

3- The linearity of response of the flame ionization detector (F.I.D.)

to trifluralin is shown in figure 2.4 for both direct injection and for thermal desorption. The relationship between trifluralin concentration and the detector response was linear.

Typical chromatograms of direct injection onto GLC column and through the Tenax-trap and headspace samples of treated and untreated Arkleston soil are shown in figure 2.5.

4- The recovery results of trifluralin from the Tenax trap based on direct injection are shown in Table 2.2. The nearest recovery value was used as the correcting factor for the daily trapped amount.

Table 2.2 The recovery of trifluralin from the Tenax trap using the thermal desorption technique.

Trifluralin (ug)	% Recovery \pm SD
0.05	92.34 \pm 2.01
0.10	96.95 \pm 1.41
0.20	96.20 \pm 1.30
0.30	98.33 \pm 1.91
0.40	98.34 \pm 1.41
0.50	95.73 \pm 1.40
1.00	95.55 \pm 0.81
5.00	94.21 \pm 1.71
10.00	96.23 \pm 1.20
20.00	95.01 \pm 0.45

5- The effect of storage period under different temperatures on the recovery of trifluralin from the Tenax trap was assessed. The results of the assessment are given in Table 2.3. The calculation of the recovery values was based on the mean of the peak areas of five fresh injections which were carried out at the same time as the stored trap analysis. The results show that, the trapped sample of trifluralin vapours can be stored in a fridge ($5^{\circ}\text{C} \pm 1$) for up to five days with no significant loss while for the same period at room temperature (20 ± 2) a significant loss was observed. In the case of the 10-day storage period at fridge temperature the loss in recovery was slightly significant while at room temperature it was much more significant. The loss in recovery could be put in the following order 10 days/room temperature > 5 days/room temperature > 10 days/fridge > 5 days/fridge.

Table 2.3 The effect of storage period under different temperature on the recovery of trifluralin from Tenax traps.

Tenax trap No.	% Recovery of trifluralin at			
	5°C±1 (fridge)		20°C±2 (room temperature)	
	after days		after days	
	5	10	5	10
1	100.85	95.10	91.27	79.06
2	98.63	98.71	91.97	78.67
3	98.13	99.95	92.66	75.41
4	98.06	90.75	90.91	77.74
5	95.03	90.49	94.61	78.48
Mean	98.14	95.00	92.28	77.87
SD	1.89	3.92	1.31	1.30

B- Volatility of trifluralin from soil

A preliminary large scale study using Arkleston sandy loam soil was carried out in three replicates to determine the effects of temperature and soil moisture content on trifluralin volatility. An Iraqi clay loam soil was chosen to estimate the effect of soil type on the trifluralin volatility and acid washed sand was selected as a control treatment. Because of limitations in the size of the sample of Iraqi soil, the Iraqi soil treatment was carried out without replication.

The results of trifluralin volatility from different soils under different temperatures and moisture contents are shown in Figures 2.7-2.14. The analysis of variance showed a significant difference over all soil types at 0.05 confidence level, but the LSD showed the significance was due to the acid washed sand, which is not really a normal soil while no significant difference was noted between Arkleston sandy loam soil and Iraqi clay loam soil.

Generally, the total amount of trifluralin trapped from the sand treatment was much higher than from the Iraqi soil treatment and relatively less from the Arkleston soil treatment compared with the Iraqi soil treatment under all investigated temperatures and moisture contents (Fig.2.7 and 2.8). Theoretically, the organic matter content (O.M.) of the soil effects the vapour density of trifluralin in soil and this effect reflects the volatility of trifluralin. So the O.M. content reduces the volatilization rate of trifluralin from soil. Because the investigated soils in this study varied in O.M. content, they exhibited various vapour losses. The maximum losses were 7.36, 1.70, and 0.59% of applied trifluralin from the sand (0.00% O.M.), Iraqi soil (2.8% O.M.) and Arkleston soil (7.5% O.M.) treatments respectively under field capacity moisture content and 40°C. The minimum losses were 1.61, 0.03, and 0.02% of the applied trifluralin from the sand, Iraqi soil, and Arkleston soil treatments respectively under air dried moisture content and 20°C.

These results are as expected and theoretically acceptable when compared with the information reviewed by Plimmer (1976), He found that, the diffusion coefficient decreased with increased percentage of

organic matter. The diffusion coefficient was highest in quartz sand where there is little interaction between the medium and the pesticide. In addition, Wheatley (1976) reported similar information, i.e. pesticides disappear as vapour most rapidly from sand or soils containing little organic matter and very slowly from soils that contain a large proportion of organic matter. In soils containing little O.M., adsorption onto the mineral complex, particularly clays is an important factor affecting volatilization.

Also the results are in agreement with the results found by Spencer and Cliath (1974), who explained that, as O.M. content increased the vapour density decreased. In addition, they concluded that trifluralin adsorption is a function of the O.M. content of the soil and they reviewed also many studies reporting that, the toxicity or activity of trifluralin was related to the O.M. content.

Fig.2.7 Total vapours loss of trifluralin from different soils at 20°C, under different moisture contents in 13-day period.

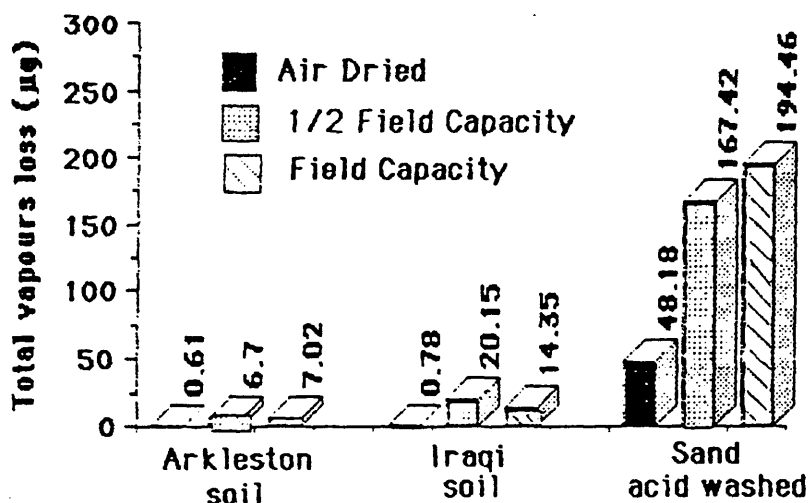


Fig.2.8 Total vapours loss of trifluralin from different soils at 40°C, under different moisture contents in 13-day period.

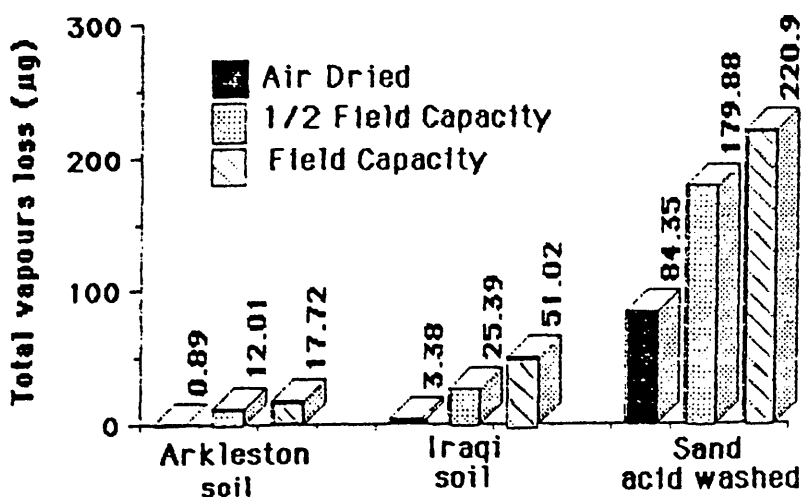


Fig.2.9 Daily trifluralin vapours loss from ARKLESTON soil, under different moisture contents and temperatures

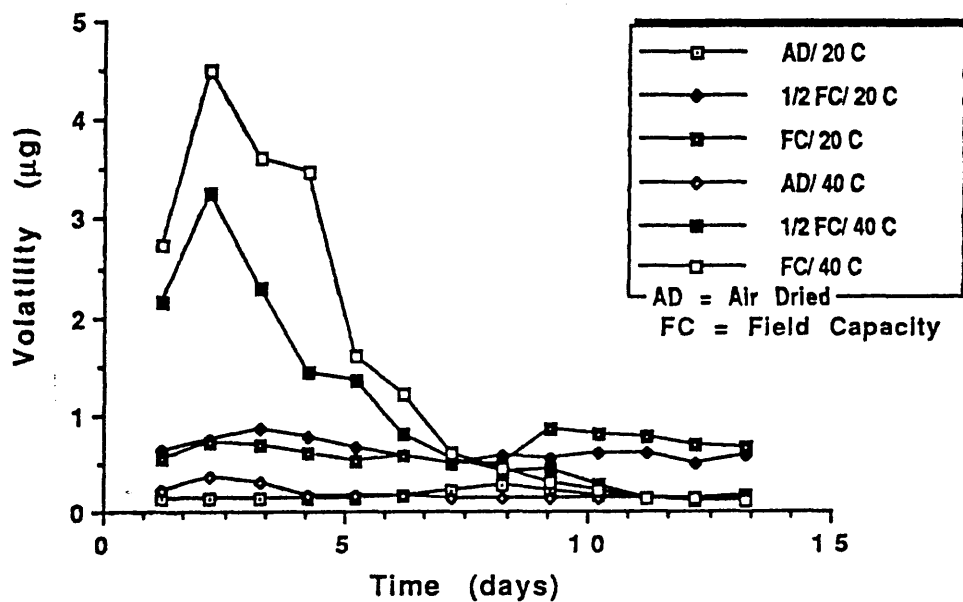


Fig.2.10 Daily trifluralin vapours loss from IRAQI soil, under different moisture contents and temperatures

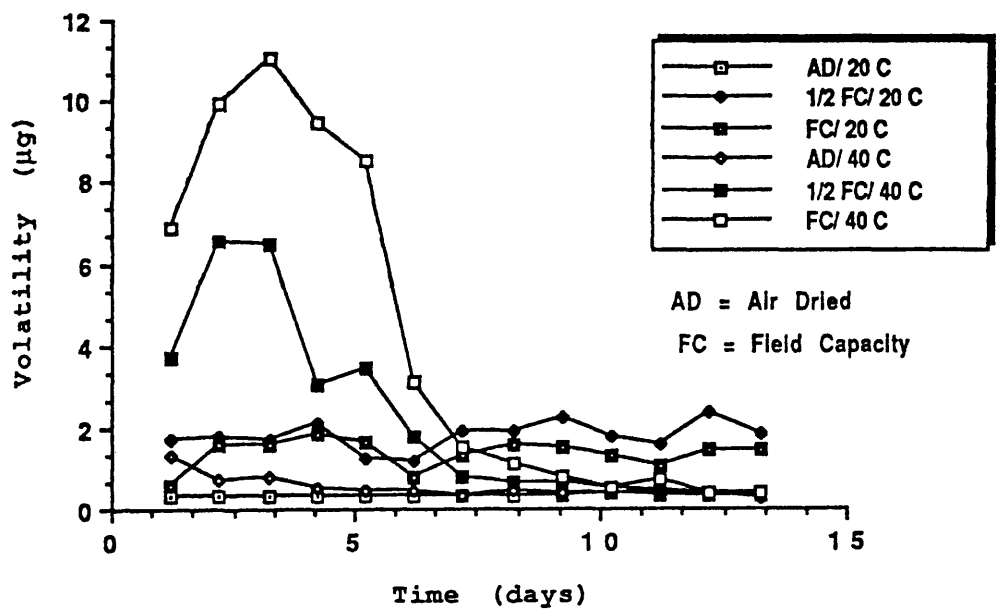


Fig.2.11 Daily trifluralin vapours loss from SAND ACID WASHED, under different moisture contents and temperatures

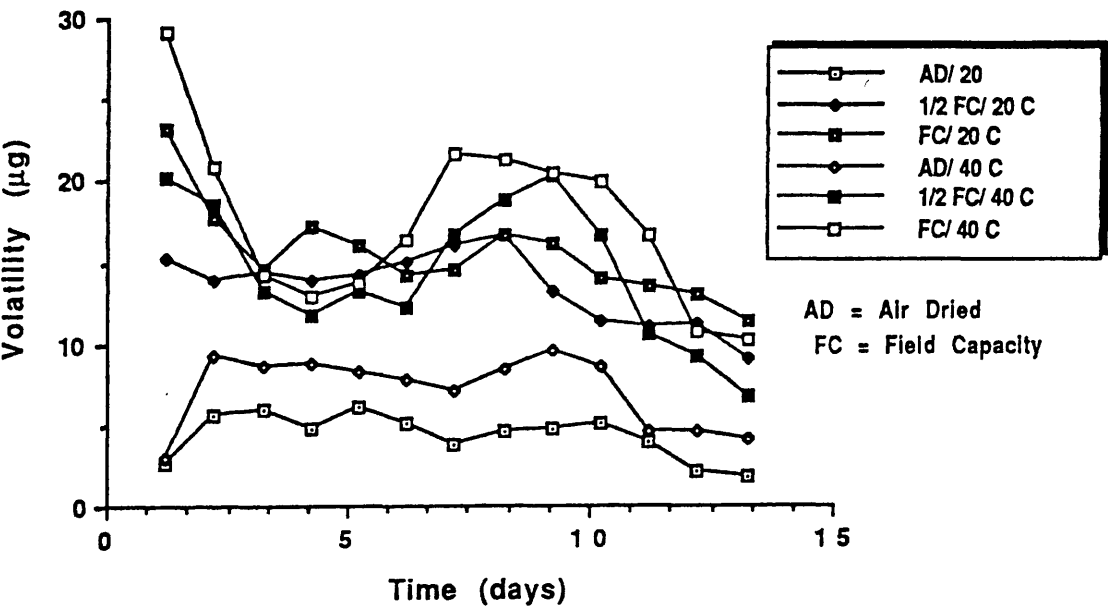


Fig.2.12 Cumulative vapour losses of trifluralin over 13-day period, from ARKLESTON soil under different moisture contents and temperatures

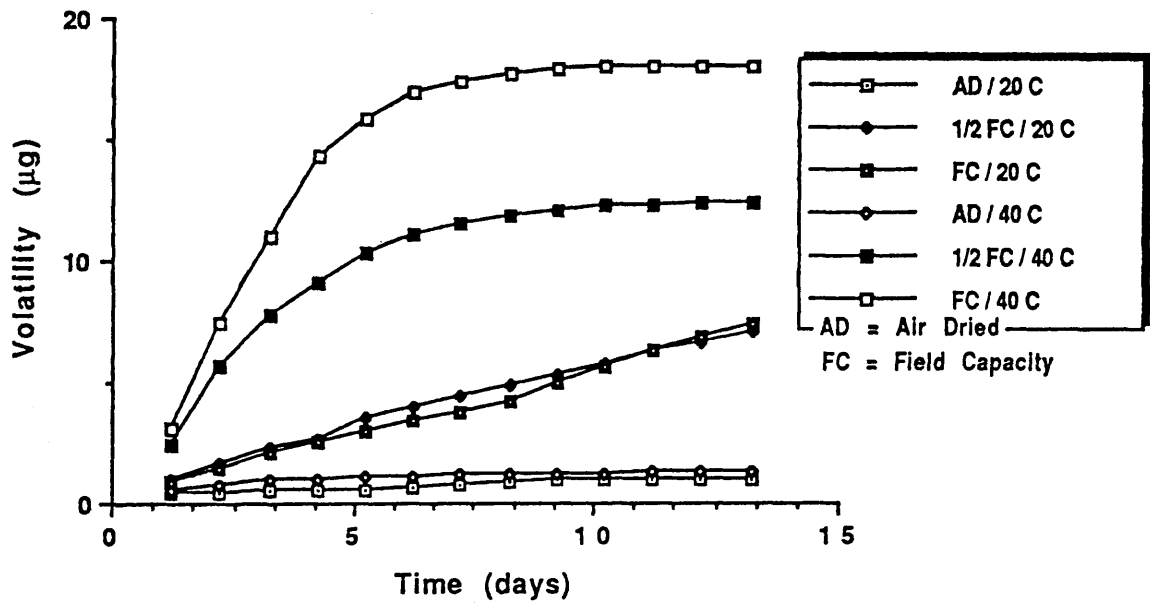


Fig.2.13 Cumulative vapour losses of trifluralin over 13-day period, from IRAQI soil under different moisture contents and temperatures

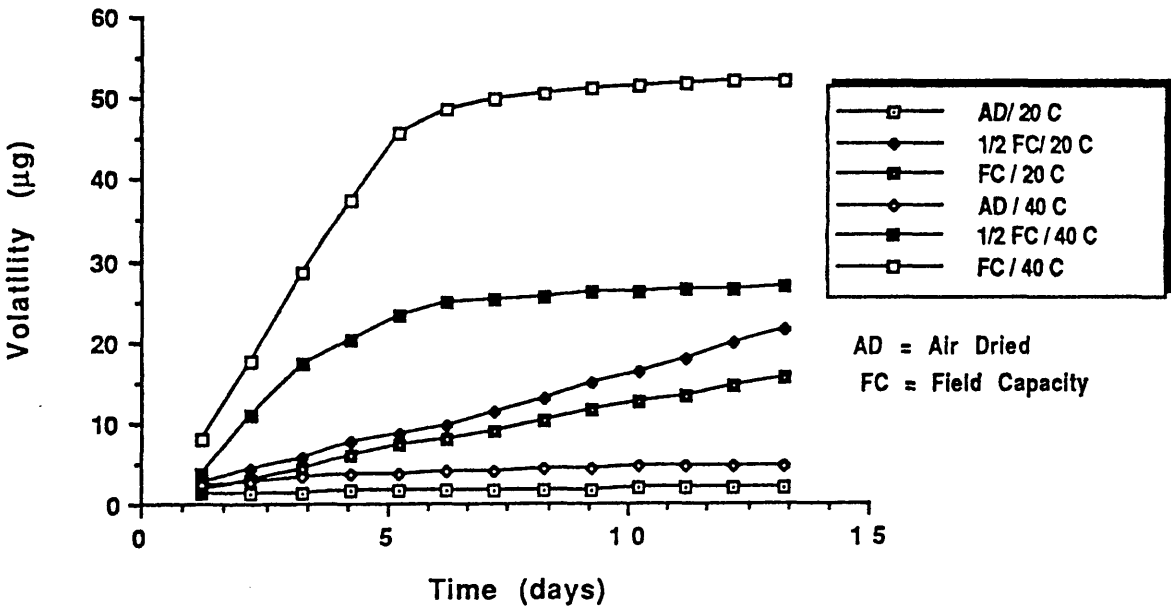
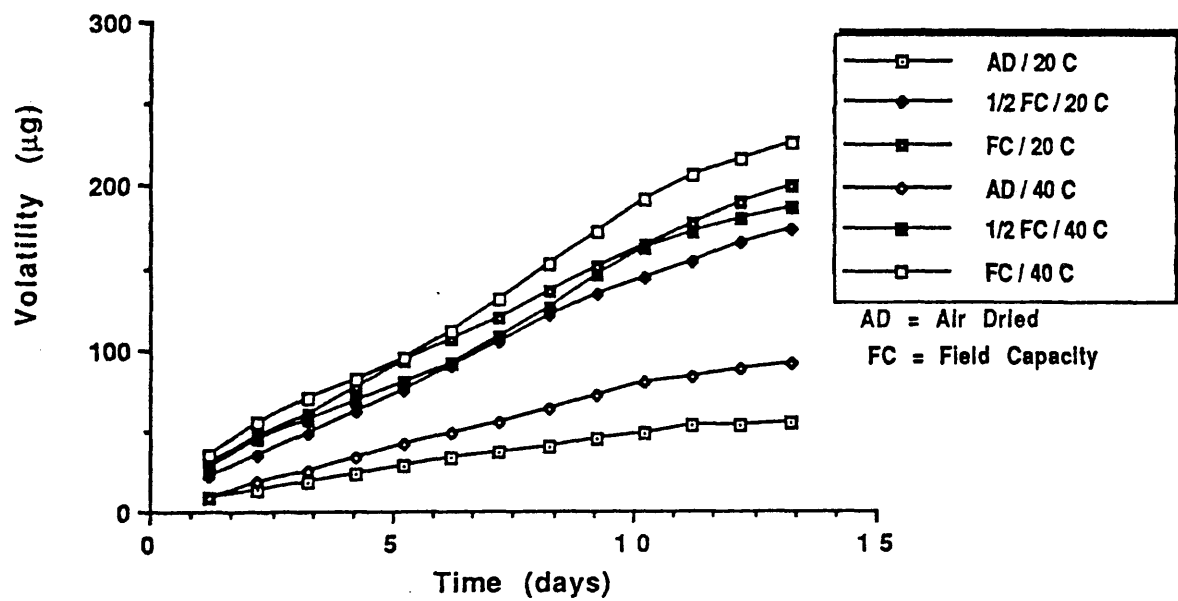


Fig.2.14 Cumulative vapour losses of trifluralin over 13-day period, from SAND ACID WASHED under different moisture contents and temperatures



C- Adsorption of trifluralin on soils

The recovery data of trifluralin from water are shown in Table 2.4.a. These data were used as a control for the trifluralin adsorption study. The trifluralin adsorption results which were corrected for the control recovery are shown in Table 2.4.b. These results are presented in graphical form in Figure 2.6.a.

The relation between the amount of trifluralin adsorbed on soil and the amount in solution was linear for all investigated soils using three levels of application. The data show the partition of trifluralin between soil and water. The partition coefficients calculated from the slope of the lines (obtained by linear regression) showed that adsorption of trifluralin was greatest on Arkleston soil (925.7), less with the Iraqi soil (487.3) and much less on the acid washed sand (5.3).

The partition of trifluralin between soil and water also can be described by use of the Freundlich isotherm equation ($x/m = KC^{1/n}$). Where x is the weight of trifluralin adsorbed on soil (ug), m is the weight of soil (g), C is the equilibrium concentration of the trifluralin in solution, and K and $1/n$ are constants. The log form of the Freundlich isotherm equation ($\log x/m = 1/n \log C + \log K$) can be used to describe the adsorption of trifluralin. By plotting $\log x/m$ against $\log C$ a straight line is obtained (Figure 2.6.b). Values for the slope $1/n$ and intercept K were obtained by linear regression. The values for K and adsorption of trifluralin by investigated soils are shown in Table 2.4.b.

The difference in trifluralin adsorption on investigated soils was significant. The means of the adsorption percentages were 4.39, 79.10, and 90.25% on sand (0.00% O.M.), Iraqi soil (2.8% O.M.), and Arkleston soil (7.5% O.M.) respectively (Table 2.4 and Figure 2.6). The results indicate that the soil O.M. content plays a significant role in the adsorption of trifluralin. Hollist and Foy (1971) found that, trifluralin was adsorbed strongly on O.M. and the effect of clay on the adsorption was small when the O.M. was removed, Clay (montmorillonite) interacted synergistically with other adsorbents to reduce phytotoxicity of trifluralin. They found also that trifluralin was adsorbed mainly by nonionic resins, confirming trifluralin has a neutral characteristic. Coffey and Warren (1969) found the same. Trifluralin was strongly adsorbed on activated carbon, about fifteen times stronger than on bentonite clay. Another study supported the view that the clay content did not correlate with the activity of trifluralin but there was a significant correlation with O.M. content (Horowitz et al., 1974).

The studies reviewed above, indicate that the O.M. content is the most effective factor on the adsorption of trifluralin and this supports what has been found in this adsorption study.

Table 2.4.a Control for trifluralin adsorption study,
recovery of trifluralin from water.

Treatment level (ug 100 cm ⁻³)	Replicate No.	Detected (ug 100 cm ⁻³)	%Recovery
30	1	22.51	75.04
	2	25.17	83.90
	3	24.17	80.56
	Mean		79.83
50	1	39.94	79.88
	2	42.52	85.03
	3	39.23	78.46
	Mean		81.12
70	1	59.85	85.50
	2	56.46	80.66
	3	58.89	84.12
	Mean		83.43

Table 2.4.b The adsorption of trifluralin by different soils.

Treatment level (ug) ¹	% Adsorption by		
	Arkleston soil ²	Iraqi soil ³	Sand ⁴
30	89.99	77.07	3.43
	91.80	79.33	4.67
	89.77	76.40	3.97
Mean	90.51	77.60	4.02
SD	0.91	1.25	0.51
50	88.66	79.04	3.78
	89.82	79.92	5.54
	91.04	77.98	4.42
Mean	89.84	78.98	4.58
SD	0.97	0.79	0.73
70	90.23	81.11	5.80
	90.37	79.64	3.11
	90.61	81.37	4.84
Mean	90.40	80.71	4.58
SD	0.16	0.76	1.11
K^5	18.64	17.13	2.06

¹30, 50, 70 ug g⁻¹ soil

²Sandy loam soil

³Clay loam soil

⁴Acid washed

⁵Freundlich constant

Fig.2.6.a Equilibrium adsorption isotherm of Trifluralin on soils.

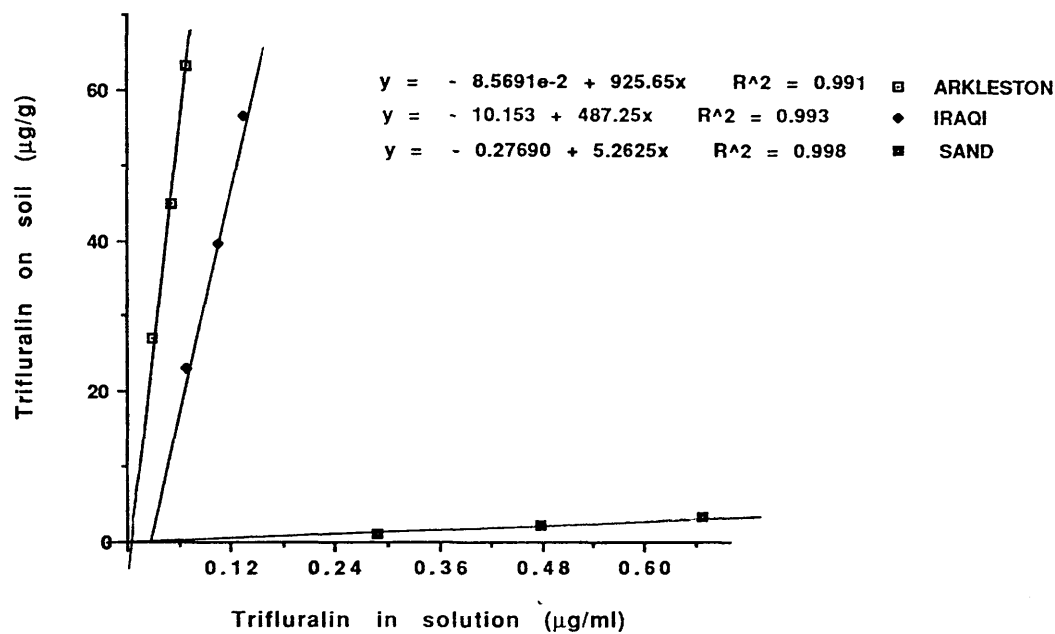
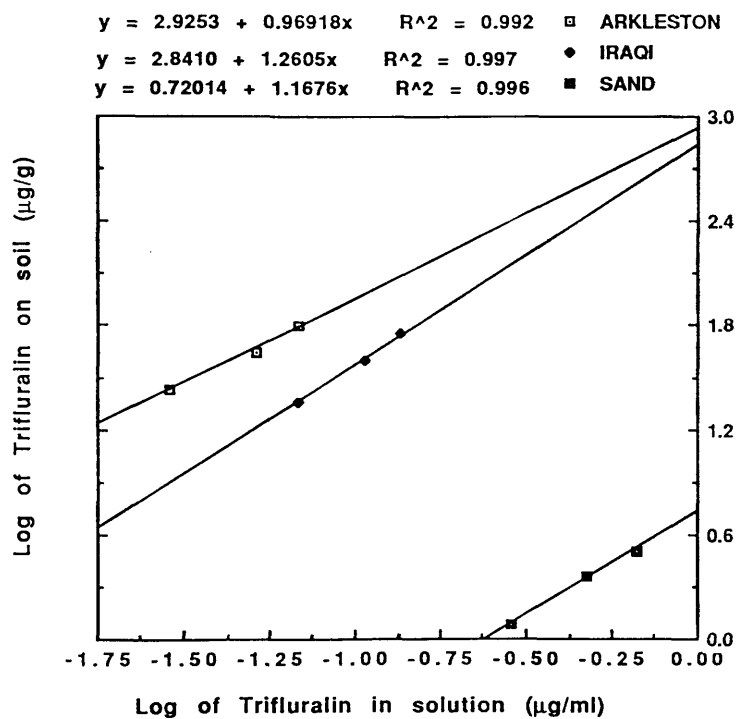


Fig.2.6.b Freundlich isotherm constant (K) of trifluralin in different soils.



The loss of trifluralin was influenced more by soil moisture content than by soil type (Ketchersid et al. (1969). This study was in agreement with this as it was found that the moisture content factor has the greatest effect on the volatility of trifluralin compared with other factors such as soil type and temperature.

The minimum volatility, within each soil in the present work, occurs in the air dried condition. The volatility increases greatly with increasing moisture content. In one circumstance, only was there an exception to this trend. In the Iraqi clay soil treatment at 20°C, the volatility was less under field capacity moisture content than under $\frac{1}{2}$ field capacity. The reason may be due to the high clay content of Iraqi soil which helps to hold the high moisture content for a longer time at 20°C compared with 40°C and this may reduce the porosity of the soil thereby causing a reduction in the trifluralin diffusion through the soil. This behaviour did not occur at 40°C under the same moisture content (field capacity) likely due to the fast water loss at this temperature.

Excessive moisture content has been reported to reduce volatility of trifluralin (Swann & Behrens, 1972). In addition, Parochetti et al. (1976) found that, in clay loam soil, losses for benefin, prof-luralin, and trifluralin decrease as moisture content exceeds field capacity. They gave an explanation that, diffusion of trifluralin decreased at soil moisture contents greater than field capacity plus subsequent reduced adsorption by soil. Also in another study (Bode et al., 1973) it was found that, the diffusion of trifluralin in silty loam soil reaches a maximum near 18% (w/w) soil moisture and decreases at higher moisture levels.

Generally, the results of this study indicate that, volatilization increased with increasing moisture content at both temperatures (20 and 40°C) in all investigated soils except in the case of the Iraqi soil mentioned above at 20°C under field capacity. These results are in agreement with what was found by Parochetti and Hein (1973) where the loss of trifluralin vapour increased rapidly as soil moisture levels increased from dryness to field capacity at temperatures of 40 or 50°C. Nash (1983) also found that, higher soil moisture contents at any given time resulted in a higher flux relative to a lower soil moisture content.

The effect of soil moisture content was very clear among the treatments within each soil type at both investigated temperatures. The effect was much more with Arkleston soil treatments than with Iraqi soil treatments and relatively less with acid washed sand treatments at both 20 and 40°C. The explanation of this finding may be due to the influence of moisture content on trifluralin adsorption on O.M. The results of the adsorption study (Table 2.4 and Figure 2.5) have shown that the adsorption of trifluralin is related to the O.M. content. The means of the adsorption values are 90.25, 79.10, and 4.39% for the Arkleston soil (7.5% O.M.), Iraqi soil (2.8% O.M.), and acid washed sand (0.0% O.M.) respectively. The competition between water molecules and trifluralin molecules on the O.M. surfaces is expected to be higher in the Arkleston soil than in the Iraqi soil and low in the acid washed sand. The adsorption behaviour will therefore be influenced depending on the moisture content. Spencer and Cliath (1974) found that, the vapour density of trifluralin is 50% greater at 19% than at 6% soil water content and the vapour density is markedly red-

uced in the drier soil. On the other hand the vapour density decreases as the O.M. content increases. In addition, Hollingsworth (1980) found that, in silt loam soil, rainfall and resultant soil moisture effects markedly influenced the volatilization of trifluralin.

Table 2.5 Water loss from soils during the study period.

Soil type	Temp. (°C)	% Initial moisture content	% Moisture contents after 13 days
Arkleston sandy loam	20	3.73 (AD) 15.80 ($\frac{1}{2}$ FC) 31.60 (FC)	4.00 13.00 25.10
	40	3.73 (AD) 15.80 ($\frac{1}{2}$ FC) 31.60 (FC)	1.67 1.72 2.12
Iraqi clay loam	20	5.59 (AD) 24.97 ($\frac{1}{2}$ FC) 49.93 (FC)	5.99 16.62 34.20
	40	5.59 (AD) 24.97 ($\frac{1}{2}$ FC) 49.93 (FC)	4.05 4.01 3.88
Sand acid washed	20	0.05 (AD) 12.35 ($\frac{1}{2}$ FC) 24.70 (FC)	0.07 1.42 12.09
	40	0.05 (AD) 12.35 ($\frac{1}{2}$ FC) 24.70 (FC)	0.06 0.07 0.06

AD = Air Dried FC = Field Capacity

The effect of water loss from treated soils especially at 40°C was very great thereby influencing the trifluralin volatility from all the investigated soils. The water losses are presented in Table 2.5. The volatility decreased rapidly after 1, 2, and 3 days from the Sand, Arkleston soil, and Iraqi soil respectively at all 40°C-treatments. These results were expected since the competition of water molecules with trifluralin molecules becomes less after lossing significant amounts of water when the adsorption of trifluralin on the adsorption sites will be greater. Water molecules compete more successfully than the pesticide molecules for the active adsorption sites and therefore moisture reduces the sorptive tendency of the pesticide. In dry soil, both water and pesticide tend to be strongly adsorbed (Wheatley, 1976). In addition, Hollist and Foy (1971) found that, increased moisture content resulted in decreased adsorption and enhanced vapour movement. The effects of soil moisture content on pesticide volatilization have been shown under controlled laboratory conditions in many studies (Bardsley et al., 1968; Spencer et al., 1969; Igue et al., 1972; Harper et al., 1976; Spencer and Cliath, 1976). These studies demonstrated that, pesticide volatilization virtually stops at low soil water contents. More recently, the importance of soil moisture content was highlighted by Nash (1983) when he measured the effects of six independent variables on the volatility of many pesticides including trifluralin. The moisture content was the most important variable affecting volatilization followed by air temperature.

Increasing the temperature from 20 to 40°C enhances the volatility of trifluralin from all investigated soil types at all moisture contents. However compared with other factors such as soil moisture content and soil type, the temperature has relatively little effect.

Theoretically, there is a relationship between diffusion and the compounds vapour pressure. Increasing the temperature increases the vapour pressure of trifluralin and since the diffusion depends on the vapour pressure, so increasing the temperature enhances the volatility.

The enhancement effect of temperature on volatility was on average not more than 1.4 and 1.7 time in sand and Arkleston soil respectively while in the Iraqi soil it was about 3 times. The explanation of these results is more likely due to the high clay content of Iraqi soil (48.3% clay) which suppresses the loss of water relatively more than in the case of the Arkleston soil (15.7% clay) and sand (0.0% clay). The high clay content may extend the period of the moisture content effect on the volatility.

Spencer et al. (1973) reviewed and discussed the effect of temperature on the volatility of pesticides from soil. The temperature may influence volatility of soil incorporated pesticides through its effect on movement of the pesticides to the soil surface by diffusion or by mass flow in the evaporating water, or through its effect on the soil water adsorption-desorption equilibrium. For these effects, also, increases in temperature are usually associated with increases in volatilization rates. However, this may not always be the case since an increase in temperature will be associated with an increase in drying rate of the soil surface.

The decrease in the volatility with time was greater at 40°C-treatments compared with 20°C-treatments (Figures 2.9 - 14) in this st-

udy. This in part may be due to the more rapid decrease in the total soil trifluralin concentration at 40°C. The rapid decrease in the rate of volatility was probably largely due to diffusion of trifluralin to the soil surface becoming the limiting factor controlling volatility as the surface soil trifluralin concentration was depleted. A similar rapid decrease in the volatilization of soil incorporated trifluralin with time was found by Spencer and Cliath (1974). They explained this as a depletion of trifluralin at the soil surface. In addition to this explanation, because rapid loss in water from soil at 40°C was much more rapid (less than air dried level) than at 20°C and since more loss in water mean more adsorption of trifluralin on adsorption sites this mainly reflects on diffusion rather than on volatility. Farmer et al. (1972) found the same behaviour at 30°C compared with 20°C when dieldrin was used.

Generally, the residues of trifluralin in the sand treatments were smaller than in the Arkleston and the Iraqi soil treatments. The reason for this would be due to the high total loss by volatility from sand compared with the other two soils.

The distribution of trifluralin residues between the top (the first 1 cm layer) and the bottom (last 1 cm layer) of the treated soil profile was investigated after a 13-day period headspace sampling exercise. The results of this investigation are given in Table 2.6.

Table 2.6 Distribution of trifluralin residues within treated soils profile after 13 days of treatment. AD = Air Dried. FC = Field Capacity.

Soil type	Temp. (°C)	Moisture content	Trifluralin residues in soil ($\mu\text{g g}^{-1}$)	
			Top	Bottom
Arkleston sandy loam	20	AD	9.76	9.75
		$\frac{1}{2}$ FC	9.24	9.44
		FC	9.14	9.43
	40	AD	9.54	9.04
		$\frac{1}{2}$ FC	8.84	8.35
		FC	8.35	7.87
Iraqi clay loam	20	AD	9.27	9.05
		$\frac{1}{2}$ FC	7.31	8.43
		FC	8.76	8.98
	40	AD	9.15	8.26
		$\frac{1}{2}$ FC	8.32	7.42
		FC	8.89	9.22
Sand acid washed	20	AD	7.05	8.30
		$\frac{1}{2}$ FC	6.56	8.09
		FC	6.16	7.77
	40	AD	7.26	7.13
		$\frac{1}{2}$ FC	6.76	6.66
		FC	6.24	6.44

The relatively big difference in the trifluralin residues between the top and bottom layers was in the sand treatments at 20°C; about 1.5 ug g⁻¹ higher in the bottom layer than in the top layer. The residues were slightly higher in the bottom layers of the Arkleston soil treatments at 20°C under ½FC and FC only and not different under air dried moisture content. These findings may be due to the relatively high vapour loss of trifluralin from the sand top layer compared with the top Arkleston layer and the low diffusion of trifluralin which is not sufficient to replace the trifluralin loss at 20°C. The situation of residue distribution at 40°C was different. In Arkleston soil the residues were slightly higher at the top layer while no difference was noted between the sand layers in residues. Since increasing the temperature enhances the diffusion of trifluralin, it may be that at 40°C the diffusion was sufficient to replace even the high loss of trifluralin vapours from the top layer at 40°C. The trend in distribution of trifluralin residues between Iraqi layers was not clear but generally was the same as in Arkleston soil except for the FC treatment at 40°C. In addition, there is a possibility of condensation of trifluralin vapour on the top layer accompanying the relatively high rate of diffusion of trifluralin at 40°C due to the difference in the temperature between the top and bottom layers of the 40°C treatments since the treated soils were incubated at 40°C and the air supply (cylinder) at the soil surface was at 20°C ± 2 (room temperature).

Solbakken et al. (1982) found a rise in residue levels of trifluralin after 4 weeks in a field experiment. They reviewed similar results and their explanation was that it was due to an upward movement of trifluralin caused by the climatic factors prior to and about the

time of sampling. Spencer and Cliath (1973) evaluated the "wick effect" and found that water loss accelerated pesticide volatilization only when adequate water was available and only after the soil surface had been depleted of the pesticide. Spencer and Cliath (1974) concluded that trifluralin volatilizes from the surface of silty loam soil at approximately the same rate as it moves upwards in the evaporating water and does not accumulate at the surface during drying.

The mean of the remaining trifluralin residue in the soil plus the amount which had volatilized was found not to be equal to the initial applied level. Nash (1983) found nearly 35% of heptachlor and trifluralin was missing in some manner and he suggested the possibility that some was lost through photodegradation. But in the present work the possibility of trifluralin photolysis taking place was eliminated because all of the vessels which contained treated soils and Tenax traps were covered completely by aluminium foil. In addition, there was no chance of microbial degradation taking place because the soils used were autoclaved. Probably the missing amount of trifluralin in this work could be due to loss by volatilization during the soil treatment stage, changing the Tenax traps, and/or adsorption on the internal glass surface. Wheatley (1976) reported that glass is slightly adsorptive.

CHAPTER 3

PHOTODECOMPOSITION OF TRIFLURALIN

3.1 INTRODUCTION

The troposphere, or lower atmosphere, is the region of the environment where the major portion of a compound that has been released into the environment usually exists if that compound has a high vapour pressure and a low solubility in water. In agricultural practice, pesticides are likely to enter into soils, air, and aquatic environments or deposit on plant surfaces. Phototransformation caused by sunlight is a very important route for the dissipation of pesticides in various environments.

Many applications of solar-chemical effects have been observed since ancient time e.g., (1) the bone disease known as rickets which has long been associated with a person's lack of exposure to sunshine (the conversion of ergosterol to vitamin D requires ultraviolet light); (2) white cloth has been left in the sun to bleach since ancient times; (3) many disease-causing bacteria are killed by sunlight; and (4) the well-known fading of organic dyes employed in the colouring of fabrics has led to extensive corrective research, one end result of which has been the successful development of colour photography (Crosby, 1976).

The chemical transformation of pesticides in sunlight show increasing significance. The photooxidation of phenoxy and phenylacetic acid herbicides results in rapid deactivation and low persist-

ence, but also limits their utility, while that of phosphorothionates lead to more hazardous products. Persistent chemicals such as DDE and PCP also undergo eventual photolysis, and even the PCB's and dioxins generated photochemically from pesticides are subject to both natural and intentional degradation (photoreduction) by light. Thus, most pesticides are affected either directly or indirectly by light with results which influence their utility and safety but also provide potential practical benefits (Crosby, 1979).

The photochemistry of herbicides and other xenobiotic compounds by sunlight has rapidly become an integrated part of studies concerning the environmental transformation of pollutants present in rivers, lakes, soil matrices and the atmosphere (Marcheterre et al., 1988). In addition, Miller and Zepp (1983) reported that the importance of environmental photolysis of pesticides and other xenobiotics has been realized in the last decade and methods for assessing these processes are continually being improved. The general goal has been to develop quantitative laboratory procedures which can be used to estimate photolysis under a variety of environmental conditions.

Light is electromagnetic in nature. The propagation of light involves the transfer of energy. The energy transferred depends on the wavelength of the light and its intensity. The shorter the wavelength, the greater the energy of the radiation.

Light energy is measured most commonly in terms of either wavelength (λ) or frequency (ν). The common units of measurement are the angstrom (\AA) (10^{-8}cm) and the millimicron (μ) or nanometer (nm) (10^{-7}cm), whereas ν is measured in vibrations (cycles) per second (Hz) or

in wave numbers (cm^{-1}).

Light energy is inversely proportional to wavelength and below a certain threshold value it is able to effect chemical transformations. The rather narrow region of the electromagnetic spectrum primarily involved in the interactions with matter is known as the ultraviolet (UV).

Ultraviolet light is considered to include wavelength between 4 and 400 nm, but most photochemical experiments have been restricted to the middle 200 - 300 nm and near, 300 - 400 nm. According to quantum theory, radiant energy occurs in discrete parcels or quanta. The energy (E) of each quantum, in ergs, is related to wavelength (cm) or frequency (sec^{-1}) by $E = hv = hc/\lambda$ where h is Planck's constant (6.62×10^{-27} erg - sec) and c is the velocity of light (3×10^{10} cm sec^{-1}). Converted into more familiar term by $E = 28,500/\lambda(\text{nm})$ kcal. The energy available to bring about direct photochemical transformations amounts to about 143 kcal mole^{-1} at 200 nm, 95 kcal mole^{-1} at 300 nm, and 68 kcal mole^{-1} at 420 nm. For comparison, the energy required to break the carbon-carbon bond in ethane is about 88 kcal mole^{-1} . A carbon-hydrogen bond in the same molecule requires about 98 kcal mole^{-1} , a nitrogen-hydrogen bond about 95 kcal mole^{-1} and a carbon-nitrogen bond about 99 kcal mole^{-1} . Although bond strengths may vary, depending on the type of molecule, physical state, and reaction mechanism, it is apparent that UV light is sufficiently energetic to provide for many kinds of chemical transformations.

As electromagnetic radiation, light is a form of energy and the individual particles or quanta possess energy that depends on the wav-

elength of the light. More energy is supplied by light quanta as the wavelength of the light decreases.

In the primary process, each quantum of light absorbed excites one molecule. Primary processes are those involving an excited electronic state of the molecule and include the initial act of absorption. The quantum yield of a process is defined as the number of moles of resultant product divided by the number of einsteins of light absorbed. Dissociation of a covalent bond often affords a pair of free radicals, which then react chemically and may initiate chain reactions.

Quantum energy continues to fall off as wavelength increases. In the comparatively simple type of compounds represented by the large majority of herbicides, light of wavelength greater than about 450 nm (blue-violet of the visible spectrum), representing energies less than $65 \text{ kcal mole}^{-1}$, would not be expected to bring about chemical changes under most circumstances even if the compounds were extremely efficient at absorbing energy in this region.

Energy absorption is the prime requisite for a photochemical reaction. In the UV region, the absorbed energy causes excitation of electrons and may result in the breakage and/or formation of chemical bonds, fluorescence, or merely loss as heat.

Radiation may be absorbed by a molecule, thereby increasing the energy of the molecule. Energy absorbed may increase the translational, rotational, vibrational, or electronic energy of a molecule. If the wavelength of the radiation imparts sufficient energy to interact

with the valence electrons of the molecule, an electronically excited molecule results. Energy may be lost by the excited molecule in a number of ways, one of which is chemical reaction. The result of energy absorption may be homolytic bond fission. Consequently, the reactions of the initially produced radicals will depend on the physical state of the irradiated compound, the solvent, and on other reactants present, such as oxygen. The particular wavelengths of light absorbed by a substance will depend on its physical state (gas phase, in solution, adsorbed on a surface, or irradiated as a pure solid).

Alternatively a reaction may be photosensitized. The energy transfer may be carried out by an intermediary i.e. a molecule which absorbs light (a photosensitizer) and by way of a relatively long-lived excited state, passes on energy to bring about the photolysis of another molecular species present in the medium.

Failure to react photochemically may result from the failure of a molecule to absorb light. Alternatively, stable excited states may be formed which dissipate energy by fluorescence, phosphorescence, or other pathways.

Most common herbicides exhibit their principal electron absorption maxima in the region between 220 and 400 nm. Trifluralin has an absorption maximum at 376 nm. Energy continues to be absorbed at longer wavelengths. Herbicides obviously absorb infrared radiation and provide infrared spectra but this comparatively low energy is generally sufficient only to increase the amplitude of vibration, rotation, or tumbling of the molecules.

Only about two-thirds of the solar energy reaches the earth's surface, the rest being absorbed, scattered, or reflected during passage through the atmosphere. The ozone layer of the upper atmosphere caused by oxygen photolysis effectively absorbs short-wavelength UV light. A wavelength of 286.3 nm is the shortest ever recorded at the earth's surface, and solar energy probably may be considered negligible below about 295 nm. Photolytic reactions in sunlight are bounded essentially by the UV cutoff of the ozone absorption spectrum (about 290 nm) at one end and the low-energy limit for the activation of bond breaking at the other. Within this narrow range, however, a wide variety of chemical transformations have been shown to occur (Plimmer, 1970; Plimmer, 1972; Crosby, 1976).

Guth (1980) reviewed many studies using different light sources such as germicidal lamps (rich in radiation between 240 and 260 nm), Westinghouse FS 40T (maximum energy output at 310 nm with 82% of the energy between 290 and 340 nm), medium pressure mercury arc lamps (240 W) immersed in double-mantled Pyrex tubes which act as filters for all radiation below 290 nm and Xenon burners which very closely approach that of sunlight if the infrared portion is filtered out.

The Grotthuss-Draper law, the first law of photochemistry, states that only radiation absorbed in a system (directly or indirectly) is effective in producing a chemical change. The lowest recorded wavelength of sunlight reaching the earth's surface is 286.3 nm. Many researchers have used 253.7 nm. As light of this wavelength represents an energy increase of $12.8 \text{ kcal mole}^{-1}$ greater than that at 286.3 nm, the results obtained solely with ultraviolet lamps emitting at 253.7 nm are of academic interest only. For example, diphenamid

exposed to high energy light is unstable while in sunlight it was stable.

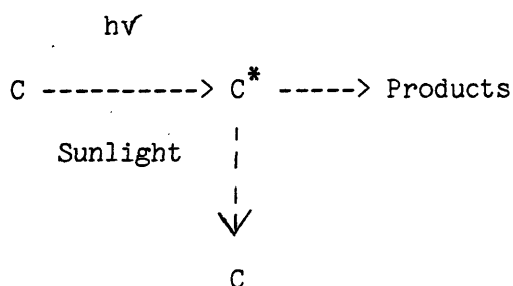
A pesticide which does not have significant absorbance in the wavelength region above 286.3 nm would not be expected to react. There are a multitude of examples in the field of pesticide photochemistry in which the law is apparently violated. A partial list of those pesticides which absorb no or very little solar energy but are significantly photolyzed by sunlight includes aldrin, dieldrin, heptachlor, carbaryl, 2,4-D, metobromuron, linuron, monouron, propanil, the pyrethroids, and paraquat (Rosen, 1972).

Photolytic transformation may include direct photodegradation, through an excited state and/or indirect photodegradation by reacting with another chemical in an excited state, namely photosensitized and photoinduced degradation. Indirect phototransformation may include the transfer of excitational energy from an excited donor molecule (sensitizer) to the acceptor molecule (quencher), which undergoes photoreactions, as well as the degradation of the chemical through its reaction with the photochemically generated intermediate species. The former process is termed sensitized photodegradation, whereas the latter is photoinduced degradation. Once a molecule is photochemically excited it can release its energy in many ways besides photochemical reactions and the efficiency of these various processes is somewhat dependent on the associated medium such as, dissolved in a liquid, in the vapour phase, adsorbed on a solid etc. (Marcheterre et al., 1988).

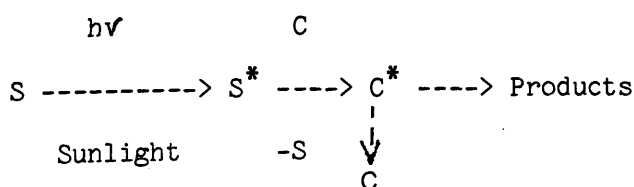
The direct and indirect photolysis reactions have occurred in

natural waters, on soils, and in the vapour phase. Indirect photolysis is the only photochemical transformation mechanism for those chemicals which does not absorb sunlight. In addition to direct photolysis and indirect photolysis, Dilling (1982) maintained other types of reaction may occur in the troposphere with various reactive species normally present in the troposphere.

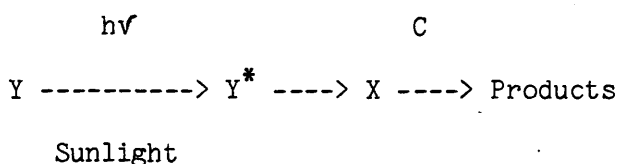
To undergo direct photolysis in sunlight, a compound (C) must absorb at least a portion of the UV or visible radiation. The absorption of sunlight, however, does not guarantee the decomposition of the compound (there are various energy-dissipating routes, which leave the absorbing species unchanged chemically).



Compounds that do not absorb sunlight directly may still undergo reactions via their excited states by an energy transfer process (indirect photolysis). A different compound that absorbs sunlight may act as a sensitizer (S), i.e., an electronic energy transfer agent. This transfer of energy to a compound (C) raises it to an excited state (C*) from which reaction may or may not occur.



Probably the most important mechanism for the destruction of organic compounds (C) in the troposphere is their reactions with reactive species (X) normally present in the troposphere [such as hydroxyl radicals (.OH) and ozone (O₃)]. These reactive species are generally formed by reactions, some of which are initiated by sunlight, of naturally occurring constituents (Y) of the troposphere.



These three types of destruction mechanisms can occur in both the gas phase and in condensed media. If the compound absorbs radiation at wavelengths longer than ~290 nm it might decompose by direct absorption of tropospheric solar radiation. If a compound does not absorb in the UV or visible region at wavelengths longer than ~290 nm, then it will not decompose by direct photolysis.

Photolysis rates are influenced by several factors involving both the chemical of interest and the environmental matrix, each of which must be considered in predicting the fate of a pesticide. The light intensity and wavelength distribution of sunlight are central factors, as are the diurnal and seasonal variations in the ultraviolet, and equally important is the spectral response of the photoreaction. The absorption spectrum and concentration of the pesticide or photosensitizer are used to calculate how rapidly sunlight is absorbed.

Using sunlight absorption rates along with reaction quantum yields, photolysis rates can be computed. Photolysis rates are also determined by physical properties of the environmental matrix in which the chemical resides. Light attenuation in soils and natural waters can substantially reduce photolysis rates. Also, vertical mixing can be an important determinant of photolysis rates, especially in the aquatic and soil environment, where light is completely absorbed in the upper layer (Miller & Zepp, 1983).

The photolytic rate and nature of the photoproducts are dependent upon the chemical properties of both the parent compound and the environmental compartment in which photolysis takes place. The probability of intercompartment movement of pesticides and their photoproducts suggests that photodegradation in the environment is a continual, dynamic process. The most important variables for each compartment include pH, dissolved oxygen, natural photosensitizers, and nucleophiles in water, common air pollutants such as the oxides of nitrogen, ozone, hydrocarbons, and particulates in the atmosphere, pH, ionic forces, organic content, and metal ions on surfaces, and dissolved oxygen and natural photosensitizers in organic films (Moilanen et al., 1975).

The specific light adsorption rate of a pesticide can be calculated by computer program (Zepp & Cline, 1977) for a particular latitude, time of day, and time of year. This calculation provides a useful measure for determining which wavelengths are most important for the direct sunlight photolysis of particular pesticides.

It is a fundamental rule of photochemistry that light must be

absorbed before any reaction can take place, and so the lesser energy represented in the sunlight spectrum could be expected to place severe restrictions on photochemistry in the environment.

Oxidation probably is the most widespread photochemical reaction of pesticides under environmental conditions. Several examples of the oxidative dealkylation of herbicides containing N-methyl groups are monuron [1,1-dimethyl-3(p-chlorophenyl) urea] demethylated to p-chlorophenylurea by light and air; diphenamid (N,N-dimethyl diphenylacetamide) monodealkylated; and triflurlin and related compounds N-dealkylated upon UV irradiation (Crosby, 1972).

Wright and Warren (1965) observed that trifluralin decomposed both in sunlight and under laboratory UV light. Decomposition was paralleled by progressive changes in the UV absorption spectrum and loss of herbicidal activity. Although photolysis proceeded on a soil surface, the reaction was much slower than when irradiation was carried out on glass plates. No products were identified.

Probst and Tepe (1969) reviewed that, photochemical decomposition is characteristic of substituted aromatic nitro compounds. Trifluralin and its related compounds in methanol and heptane solutions decomposed extensively when exposed to UV radiation. Ten trifluralin-related compounds were detected by gas chromatography after exposure of anhydrous methanol solutions containing trifluralin.

Crosby and Li (1969) reviewed that, the photoreduction of one of the nitro groups in dinitrocompounds to the amine was noted and partial photoreduction of aromatic nitro compounds to the corresponding

nitrosobenzenes has long been known. The formation of the nitroso is also consistent with the observed photodealkylation of other alkylanilines. They then concluded that, photolysis of trifluralin as well as its close relatives may be expected to produce products which are reduced and/or dealkylated. Major products from the irradiation of excess trifluralin on soil suspensions were identical to those formed in water alone at the same pH. The investigation of trifluralin degradation in aerobic soil by Probst et al. (1967) revealed some of the same products which were found in photodecomposition. Although it is possible that light could have contributed to their formation, their probable derivation from microbial action may indicate again the similarity of photolysis products to those of oxidative metabolism (Crosby, 1972).

Crosby and Leitis (1973) and Leitis and Crosby (1974) investigated the photodecomposition of aqueous trifluralin suspensions and solutions by sunlight and identified the major photolysis products which were isolated by non-destructive techniques. Trifluralin or its photoproducts were suspended in deionized or tap water (50 mg l^{-1}) and irradiated in loosely closed Erlenmeyer flasks under summer sunlight in Davis, California, for about 4 days. To obtain larger amounts of photolysis products, they irradiated 200 mg l^{-1} of trifluralin (10% aqueous methanol) at different pH in a sunlight-simulating photoreactor. A suspension of 5 g clay soil in 100 cm^{-3} of tap water (pH 6.5) was also irradiated in the photoreactor for 4 days. They found that, the photodecomposition of trifluralin was very rapid in aqueous methanol and 6 products were detectable after less than two minutes of irradiation, and 25 were observed after 3 h. The photodecomposition in aqueous suspensions, with or without soil, was about one tenth as

rapid, but the products were the same. Two products were confirmed as 2,6-dinitro-N-propyl- α,α,α -trifluoro-p-toluidine and 2,6-dinitro- α,α,α -trifluoro-p-toluidine. 2-amino-6-nitro- α,α,α -trifluoro-p-toluidine was the principal product under acidic conditions while 2-ethyl-7-nitro-5-trifluoromethyl benzimidazole was the principal product in base. In addition, 2-ethyl-2,3-dihydroxy-7-nitro-1-propyl-5-trifluoromethylbenzimidazoline and 2-ethyl-7-nitro-5-trifluoromethylbenzimidazole 3-oxide were readily detectable but were degraded by heat or further irradiation. The photochemical formation of benzimidazolines, benzimidazoles, and benzimidazole N-oxides conforms to a general mechanism which should apply to many dinitroaniline herbicides.

Nilles and Zabik (1974) studied the photodegradation of fluchloralin on sandy loam thin layers. The major reactions observed were photodealkylation and benzimidazole formation. The same photolytic N-dealkylation reaction was observed with profluralin in unpublished work reviewed by Guth (1980) on sandy and silty loam soil surfaces. In addition, oxidation of the trifluoromethyl group to the corresponding carboxyl derivative and the formation of non-extractables was found but only in the slightly alkaline sandy soil.

The model system of the photochemical demethylation of α,α,α -trifluoro-2,6-dinitro-N-methyl-p-toluidine in n-heptane bubbled with nitrogen with UV source for 3 h resulted in the formation of formaldehyde and α,α,α -trifluoro-6-nitro-2-nitroso-p-toluidine. Propionaldehyde was identified in a similar irradiation of a monopropyl derivative of trifluralin and the photoproduct, α,α,α -trifluoro-6-nitro-2-nitroso-p-toluidine was also identified (McMahon, 1966).

Butralin was more photostable than trifluralin or dinitramine, but 4-tert-butyl-2-nitro-6-nitrosoaniline was produced as a major product. In addition, the mixture contained the dealkylated product 4-tert-butyl-2,6-dinitroaniline. Analysis of minor components suggests two pathways of photodecomposition which can operate simultaneously. The major pathway involves excitation of the nitro group with subsequent reductions, followed by oxidation of other reactants. A minor pathway consists of displacement of a nitro group by a hydroxyl group. Cyclization to a benzimidazole, as occurs with trifluralin and dinitramine, is blocked by the branching effect of the N-sec-butyl group in the parent molecule and represents an exception in this series of compounds reported to date (Plimmer and Klingebiel, 1974).

Moilanen et al. (1975) reported that, dissolved oxygen can alter the photolysis of trifluralin. Under aerobic conditions, both oxidation and cyclization occur, producing trifluralin and 2,6-dinitro-N-propyl- α,α,α -trifluoro-p-toluidine which is rapidly converted to other products. Under anaerobic conditions, only cyclization occurs, resulting in 1-propyl-2-ethyl-7-nitro-5-trifluoromethylbenzimidazole which accumulates since it is stable under these conditions. The photolysis rate is approximately ten times faster in the presence of air.

Exposure of trifluralin in hexane or methanol to laboratory UV light for 24 h revealed rapid degradation. Seven products were detected but only five products were identified. The identified products contained dealkylated and reduced derivatives of trifluralin in addition to an unexplained rearrangement of the functional groups (nitro and trifluoromethyl). Trifluralin was found to be almost completely degraded within a 7.5 h period. To gain possible identification of

the degradation products, a trifluralin solution was exposed to UV light for 3 h (Harrison & Anderson, 1970).

Sullivan et al. (1980) confirmed that azoxybenzene and azobenzene derivatives also are formed by the photolysis of trifluralin after these derivatives were found by Golab et al. (1979) in soil. Three azoxybenzene derivatives, N-propyl-2,2'-azoxybis(α,α,α -trifluoro-6-nitro-p-toluidine), 2,2'-azoxybis(α,α,α -trifluoro-6-nitro-N-propyl-p-toluidine), and 2,2'-azoxybis(α,α,α -trifluoro-6-toluidine) and two azobenzene derivatives, N-propyl-2,2'-azobis(α,α,α -trifluoro-6-nitro-p-toluidine), and 2,2'-azobis(α,α,α -trifluoro-6-nitro-N-propyl-p-toluidine) have been identified as products from UV photolysis of 25 g trifluralin in benzene. The solution was purged with nitrogen for one hour before irradiation. Chemical reduction of the azoxybenzene yielded numerous products, including the corresponding azobenzene and hydrazo derivative [1,2-bis(α,α,α -trifluoro-2-amino-3-nitrolyl) hydrazine].

Attention has been given to photolysis in the atmosphere also, for example, the vapour-phase photolysis of trifluralin was reported in great deal in the literature.

Trifluralin proved to be volatile from soil especially after irrigation or rainfall. Laboratory experiments indicated that trifluralin vapour was very susceptible to photolysis. In the field experiment, the expected dealkylation and cyclization proceeded even more rapidly than in the photoreactor. Photolysis of trifluralin in the presence of ozone revealed a sharp increase in breakdown rate and the predominance of the N-dealkylated photoproducts. However, given its

abundance of oxygen, sunlight, and time, the atmosphere may convert the world's pesticides to harmless inorganic fragments (Crosby, 1979).

Trifluralin vapour photodecomposed to a number of products in a laboratory vapour-phase reactor which simulated sunlight conditions. Short term irradiation produced primarily a mono-dealkylated product, while longer irradiation (12 days) resulted in mono and didealkylated benzimidazole products. The didealkylated benzimidazole product was resistant to further photolysis while all others were photolabile. Following the completion of the laboratory photolysis Seiber et al. (1975) carried out several field experiment to check the laboratory results. Collected air samples contained mostly trifluralin, traces of dealkylation products and traces of both benzimidazoles. They considered three potential routes of photoproduct formation: via photolysis of trifluralin vapour in the atmosphere; via photolysis of trifluralin on the soil surface followed by volatilization; and via photolysis of trifluralin on air-suspended dust. The importance of these routes depends not only on the relative photolysis rates at the appropriate sites, but on transport to the sites as well. The field-test data indicate that photolysis of trifluralin at the soil surface followed by volatilization must predominate.

A laboratory apparatus was developed to provide a beam of collimated UV light in a suitably designed reaction chamber. Trifluralin was vaporized within the chamber and subjected to vapour-phase photolysis for 4 days at 35°C. The amount of trifluralin exposed to the UV light in this apparatus was estimated as 2.34% of the total. Several degradation products were observed in the gas chromatographic analysis of the exposed reaction mixture. The major photolyzed product was the

monodealkylated product, α,α,α -trifluoro-2,6-dinitro-N-propyl-p-toluidine, identified by mass spectrometry with an authentic model compound. The second photoproduct (m/e 259) was the benzimidazole, 2-ethyl-7-nitro-5-trifluoro-methylbenzimidazole, which resulted from the cyclization of the nitro group with the α -carbon of the propyl group of α,α,α -trifluoro-2,6-dinitro-N-propyl-p-toluidine (Crosby & Moilanen, 1972).

Under flow conditions with light >300 nm, dry air, and < 10 ppb O_3 , trifluralin decomposed with a half-life of 117 min. The half-life in the presence of 1-3 ppm O_3 was 47 min in the light and 12.5 days in the dark. No reaction occurred in the dark in absence of O_3 (Woodrow et al., 1978). Photochemical N-dealkylation of amines appears to be a free-radical oxidation by atmospheric oxygen (Seiber et al., 1975).

Pesticides in practice can be introduced into aqueous systems, onto the soil surface, onto plant surfaces or introduced in the air by volatilization from application sites or by drifting during application. Since trifluralin is expected to be found in these environments, then photolytic transformation of trifluralin by sunlight can take place in these environments.

In this work trifluralin was exposed to UV light using a Pyrex filter to avoid the wavelengths below ~ 290 nm which do not reach the earth surface. The exposure of trifluralin was carried out in various media such as water and organic solvents (methanol, n-hexane, and acetonitrile). The reason for using these chosen media were, as mentioned above, trifluralin can be found in aqueous or organic media such as soil particles, on the dust in the atmosphere or on the plant

surfaces. In addition, trifluralin was irradiated in the presence of some additives such as the free radical scavengers, 4-aminobenzoic acid and potassium thiocyanate, pigments and dyes such as chlorophyll, methylene blue, and crystal violet, and the surfactant Tween 20 which are either present or else similar possible compounds are in the environment.

The aims of this study were (1) to assess the rate of trifluralin photodecomposition in different media, (2) to measure the effect of the chosen additives on trifluralin photolysis rate since the possibility exists of their presence in the environment, in addition, and (3) an attempt was carried out to identify possible photoproducts which could vary in amount from one medium to another.

3.2 EXPERIMENTAL

3.2.1 Chemicals

Trifluralin 99% was purchased from Alltech Associates/Applied Science (Carnforth, U.K.), The emulsified concentrated formulation of trifluralin (Tristar, 48% EC) was supplied by Pan Britannica Ltd (Essex, England).

4-aminobenzoic acid (PABA) 99% was purchased from BDH Chemicals Ltd (Poole, England).

Crystal violet 95% was purchased from Raymound A. Lamb (London, England).

Methylene blue (3,9-bisdimethylaminophenazothionium chloride) was purchased from Aldrich Chemical Company Ltd (Gillingham-Dorset, England).

Potassium thiocyanate 100% and Tween 20 (Poloxyethylene sorbitan monolaurate) were obtained from Koch-Light Laboratories Ltd (Colnbrook Bucks, England).

Crude chlorophyll was extracted by methanol in the laboratory from grass.

Organic solvents such as acetone, methanol, and dichloromethane were used as Analytical Grade (May & Baker Ltd, Dagenham, England) n-hexane and acetonitrile were HPLC grade (Bathburn Chemicals Ltd, Wakerburn, Scotland).

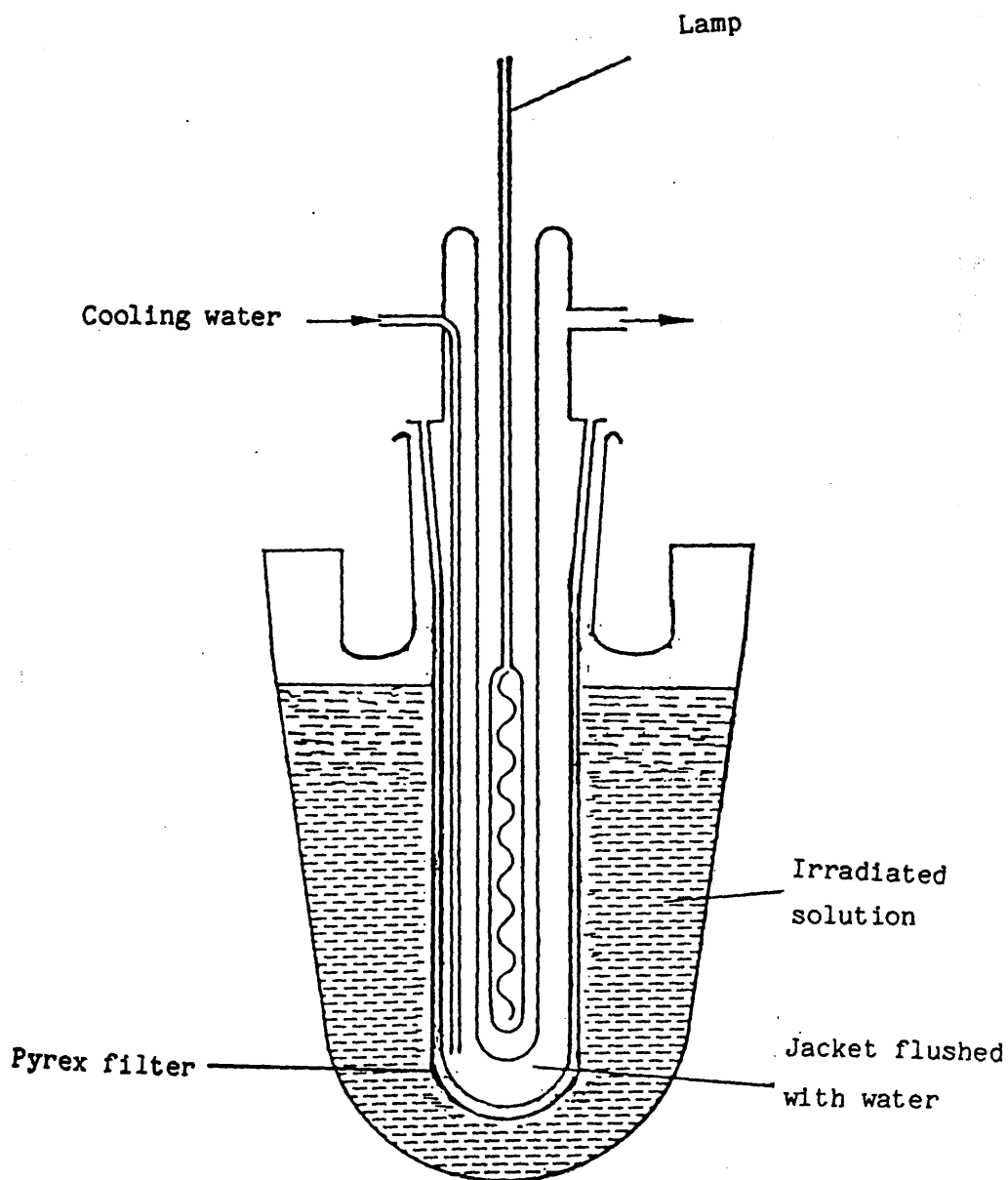
Silica gel G with ~13% gypsum for TLC was purchased from Merk, Switzerland.

All other chemicals used were Analytical Grade.

3.2.2 Irradiation

A 1 L solution of trifluralin was subjected to artificial light photolysis. The photoreactor was a medium pressure mercury vapour Hanovia lamp (Engelhard Hanovia Lamp Ltd, England) housed in a double jacket quartz immersion well in a 1 L capacity reaction vessel. The double-walled quartz well containing circulating water was used as a jacket surrounding the lamp to prevent heat transfer to the solution being irradiated. A Pyrex tube was used as a filter to prevent radiation of wavelengths shorter than ~ 290 nm from reaching the sample. The solution was stirred during the exposure period by a magnetic bar. The photoreactor is shown schematically in figure 3.1.

Fig.3.1 Photoreactor.



3.2.3 Photodecomposition rate assessment

100 mg trifluralin were dissolved in 1 L of chosen organic solvent (n-hexane, methanol, or acetonitrile) or distilled water, using 2% methanol to enhance the solubility of the trifluralin which is < 1 ppm soluble in water. In addition, 0.21 cm³ of EC formulation of trifluralin (Tristar 48% EC) which is equal to 100 mg active ingredient were irradiated in 1 L distilled water. This concentration of trifluralin was chosen as it gave convenient aliquots for analysis.

The solutions were irradiated over 3 h. Samples of 5 cm³ were withdrawn at zero time and at intervals of 10, 20, 30, 45, 60, 90, 120, 150, and 180 min. The samples were analysed by gas chromatography using the same conditions mentioned in Chapter 2 except a temperature programme was adopted to separate trifluralin from its photoproducts. The temperature programme range was from 165 to 210°C at a rate of 2°C min⁻¹ and held at 210°C for 10 min.

The remaining amount of trifluralin in each sample was determined as a percentage based on the detected trifluralin amount in the zero time sample (before exposure). The photolysis rate plot was obtained by plotting the percentage of remaining trifluralin against time.

3.2.4 Effect of some additives on the trifluralin photolysis rate

The chosen additives were added individually to a methanol solution of trifluralin at equal molar ratios except for chlorophyll(5

cm³) to assess their effect on the photolysis rate of trifluralin. The additives were 4-aminobenzoic acid (PABA), potassium thiocyanate, Tween 20, methylene blue, crystal violet, and chlorophyll.

The procedure mentioned in Section 3.2.3 was followed to measure the photodecomposition rate of trifluralin.

3.2.5 Photoproducts separation and identification

Trifluralin photoproducts in n-hexane, methanol, and distilled water were subjected to separation and identification.

After 3 h of exposure the irradiated solutions were concentrated to 10 cm³. Hexane and methanol solutions were evaporated using a vacuum rotary evaporator at 35°C while the water solution was extracted three times by partitioning with dichloromethane (500 cm³ each) then the dichloromethane extract was passed through sodium sulphate(anhydrous) and evaporated to dryness. The residues were collected in 10 cm³ methanol.

Thin Layer Chromatography (TLC) was used to separate the photoproducts of trifluralin. TLC was carried out on 20 * 20 cm glass plates coated with 0.5 mm of silica gel G containing 13% gypsum. The prepared TLC plates were activated at 110°C overnight before use. The concentrated solutions were applied to the preparative TLC plates followed by development with n-hexane:acetone (3:1) to separate the photoproducts. To avoid overlapping bands, the TLC plates were developed twice in the same solvent system. The resulting colour bands

were recognized by visual observation. The bands were scrapped off then extracted with warm acetone. The procedures of separation and band extraction were modified from Leitis and Crosby (1974). The acetone extracts were concentrated using a stream of nitrogen to dryness then the residues were dissolved in 1 cm³ methanol.

The separated photoproducts were characterised by mass spectrometry, low resolution electron impact (70 ev) with direct inlet technique. GC-MS with seimipolar column was used for some photoproducts. The identification was by comparison of the mass spectra of trifluralin degradative products with the available literature while some were deduced from their mass fragmentation patterns.

3.3 RESULTS AND DISCUSSION

The rate of trifluralin photolysis was estimated by detection of the amount of trifluralin remaining in solution at different intervals. The rates of loss by photolysis in different media, viz acetonitrile, n-hexane, methanol, and distilled water, are presented in Figure 3.2. The rate of photolysis was more rapid in the n-hexane and less in methanol and distilled water and much less in acetonitrile. The trifluralin photolysis could be fitted to a first order equation $dC/dt = -kC$, where C = concentration, t = time, and k is the first-order rate constant. The first-order equation can be expressed in an integrated form $C/C_0 = e^{-kt}$. Where C_0 = concentration at time zero. Taking the natural log (Ln) of this equation gives $\ln C/C_0 = -kt$ which describes a linear relationship. Plotting $\ln C/C_0$ against t gives a straight line with slope $-k$. The

half-life can be calculated from the rate constant using the equation $t_{1/2} = \ln(2)/k$. The half-life of trifluralin in different media and in methanol with different additives were obtained by plotting the natural logarithmic values of the remaining trifluralin against time and applying linear regression to obtain the rate constant of photolysis. The half-life data are given in Table 3.1. After 3 h of exposure the remaining amounts were 15.79, 35.73, 46.01, and 57.65% and the half-lives were 1.10, 2.05, 2.62, and 3.79 h in n-hexane, methanol, distilled water, and acetonitrile respectively. The reason for this differentiation in photolysis rates may be due to the hydrogen-donating properties of these different media. Since the reduction reaction is important in the photolysis of trifluralin, the availability of hydrogen ion in the medium effects the photolysis rate of trifluralin. As Marcheterre et al. (1988) reviewed that acetonitrile is a poor hydrogen donor compared with other solvents, the photoreduction rate of trifluralin is expected to be higher in n-hexane which is a relatively good hydrogen donor and less in the acetonitrile which is poor at donating hydrogen. Moreover, the dimerization reaction depends on the reduced trifluralin derivatives. This explanation is in agreement with reviewed work by Marcheterre et al. (1988) which demonstrated that photoreduction of nitrofen in isopropyl alcohol (an efficient hydrogen donor) was enhanced, whereas this process was greatly diminished in acetonitrile (a poor hydrogen donor).

Fig.3.2.a The rate of trifluralin photolysis in different media.

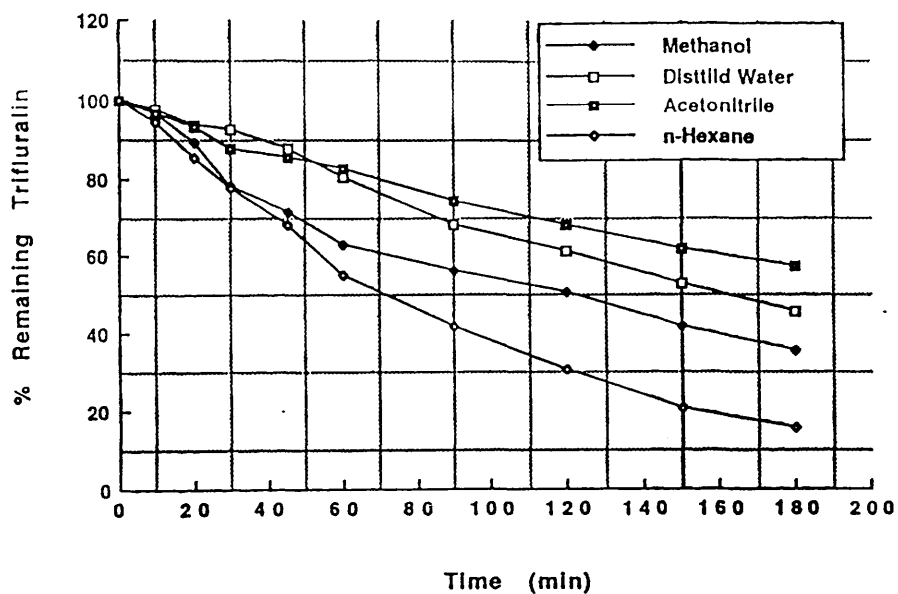


Fig. 3.2.b

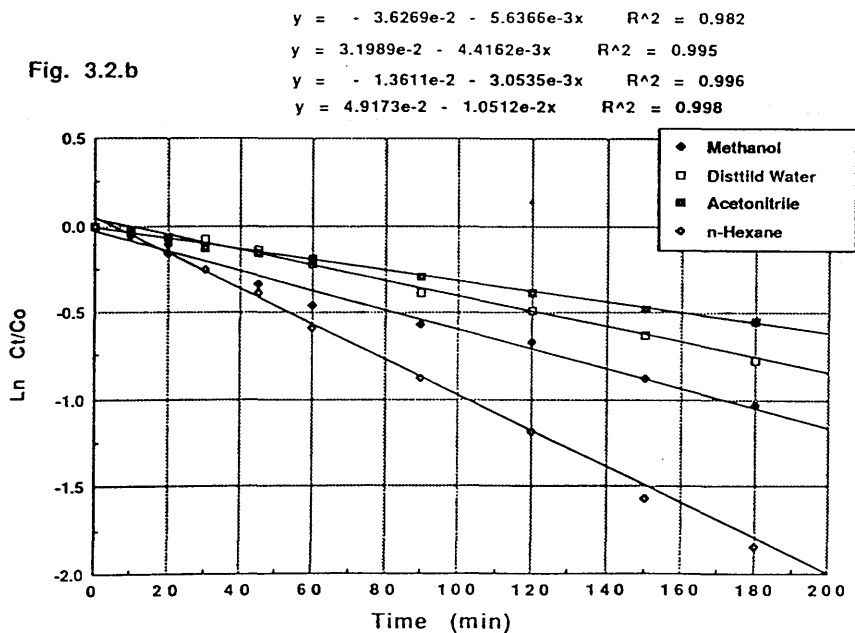


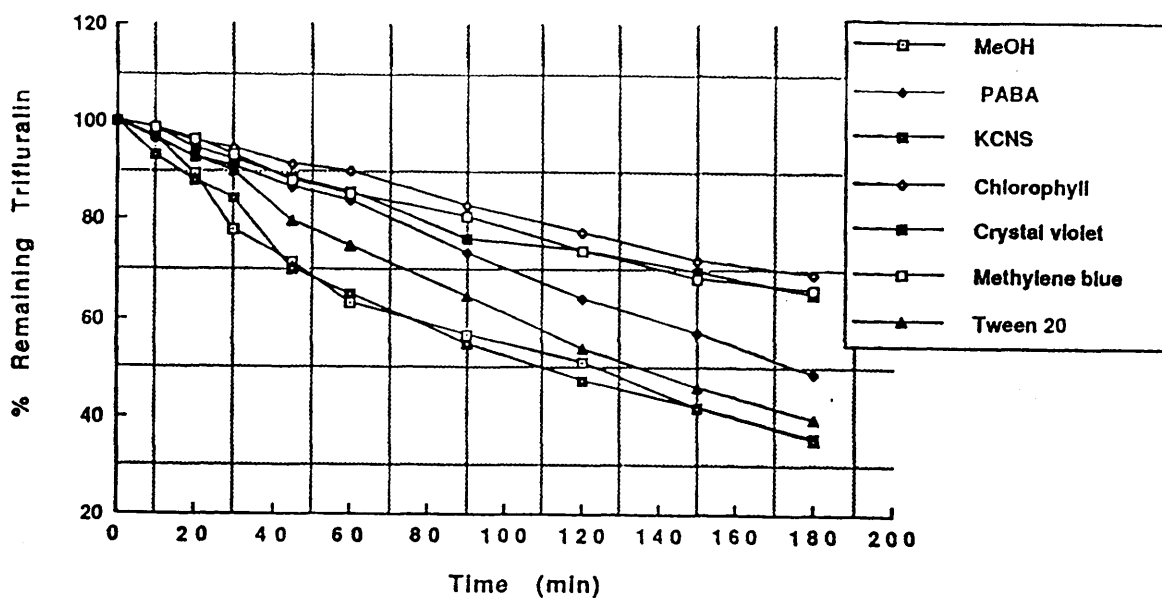
Table.3.1 Rate constant (k) and the Half-life ($t_{\frac{1}{2}}$) of irradiated trifluralin to UV (~ 290 nm) in different media and in methanol with some additives.

Medium	k (hr^{-1})	$t_{\frac{1}{2}}$ (hr)
n-hexane	0.0105	1.10
Methanol	0.0056	2.05
Dist. water	0.0044	2.62
Acetonitrile	0.0031	3.79
EC ¹ in dist. water	0.0013	8.63
Methanol + KCNS	0.0058	1.99
Methanol + Tween 20	0.0005	2.30
Methanol + PABA	0.0039	2.94
Methanol + Crystal violet	0.0025	4.70
Methanol + Methylene blue	0.0025	4.73
Methanol + Crude Chlorophyll	0.0021	5.39

¹ EC = Emulsifiable Concentrate.

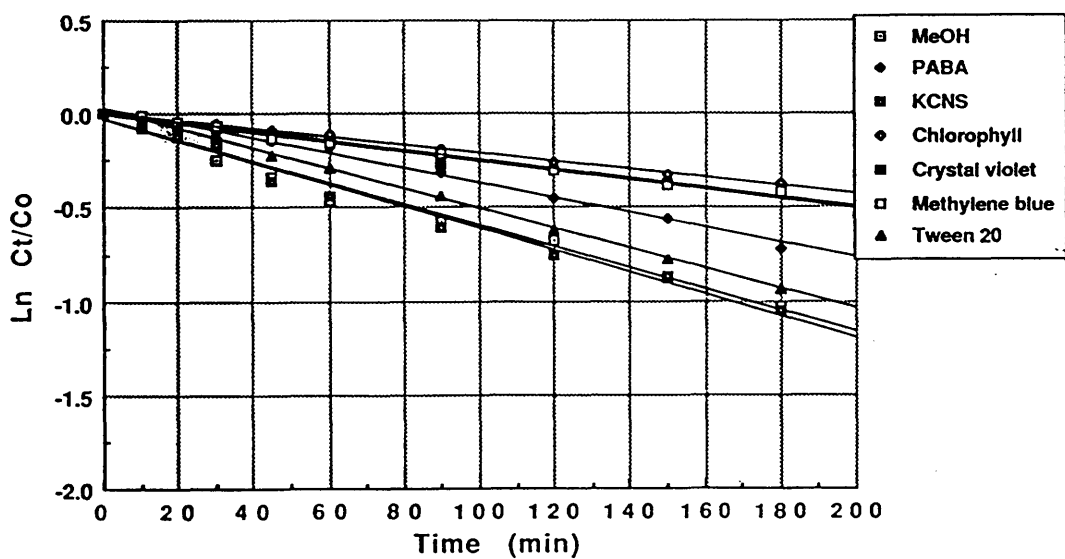
The results of the effect of various additives on the photolysis rate of a methanol solution of trifluralin are shown in figure 3.3.

Fig.3.3^a The effect of some additives on the trifluralin photolysis rate in methanol.



$$\begin{aligned}
 y &= -3.6410e-2 - 5.6395e-3x & R^2 &= 0.982 \\
 y &= 1.9826e-2 - 3.9268e-3x & R^2 &= 0.991 \\
 y &= -3.4719e-2 - 5.7986e-3x & R^2 &= 0.987 \\
 y &= 6.2330e-3 - 2.1426e-3x & R^2 &= 0.997 \\
 y &= -6.9028e-3 - 2.4609e-3x & R^2 &= 0.987 \\
 y &= -6.5319e-4 - 2.4452e-3x & R^2 &= 0.992 \\
 y &= 2.3037e-2 - 5.2882e-3x & R^2 &= 0.998
 \end{aligned}$$

Fig. 3.3.b



The crude chlorophyll extract exhibited the greatest effect in reducing the trifluralin photolysis rate. The effects of methylene blue and crystal violet were very close to the crude chlorophyll extract effect. KCNS had no effect on the trifluralin photolysis rate while the PABA and Tween 20 reduced it slightly. After 3 h of exposure, the remaining amounts of trifluralin were 35.7, 35.2, 39.4, 48.5, 64.86, 65.93, and 68.92% while the half-lives were 2.05, 1.99, 2.30, 2.94, 4.70, 4.73, and 5.39 in methanol alone, and in the presence of KCNS, Tween 20, PABA, crystal violet, methylene blue, and crude chlorophyll respectively. These findings with chlorophyll, methylene blue, and crystal violet possibly are due to scattering of radiation caused by these pigments. Miller and Zepp (1983) reviewed that photolysis on soils is slow and reasoned that photoexcited pesticides are quenched by pigments in the soil.

However, chlorophyll, methylene blue, and crystal violet were reported as photosensitizers for photooxidation of many pesticides (Lykken, 1972; Kulshrestha & Mukerjee, 1986; Marcheterre et al., 1988). The reason why these pigments did not enhance the photolysis rate of trifluralin may be, the oxidative dealkylation process is not so important as the reduction process in the photodecomposition of trifluralin. In addition, Ivie and Casida (1971) found that an aqueous suspension of spinach chloroplasts are effective in accelerating the photodecomposition of 6 out of 23 radiolabelled pesticides, the dinitrophenol derivative being one of them. They found also that purified chlorophylls a and b were sensitizers under these conditions but they were not as effective as an equivalent amount of chloroplasts.

The effect of formulation of trifluralin on its photolysis rate in distilled water was also investigated in this work. The results of this investigation are shown in Figure 3.4 and Table 3.2. The photolysis rate was much more in the 99% pure state compared with the emulsifiable concentrate formulation. After 3 h of exposure the remaining amount of trifluralin were 46.01 and 76.80% while the half-lives were 2.62 and 8.63 h in the case of pure and formulated samples respectively. The reduction in photolysis in the case of the EC formulation may be due to several factors-solvent, surfactant or some additives which are used in the manufacture of the formulation. Usually the manufacturer adds some additives to regulate the persistence of the pesticide under practical conditions. However, it is apparent that trifluralin has little opportunity to occur in the pure state in the environment. Typically, it is introduced as a dilute solution in water with organic solvent and surfactant.

Fig.3.4.a The rate of trifluralin photolysis in distilled water.

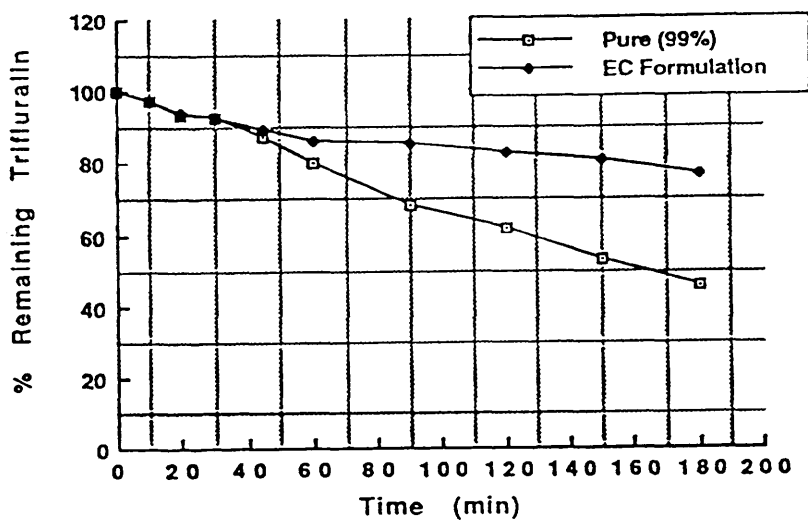
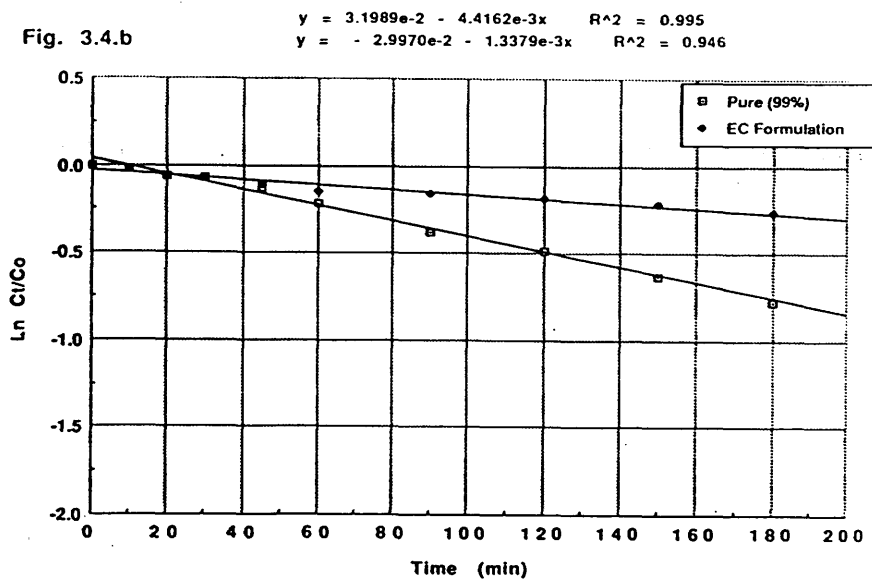


Fig. 3.4.b



Three media, n-hexane, methanol, and distilled water were selected to identify possible trifluralin photoproducts which could be formed in these different media.

In general, the identified photoproducts of trifluralin in this work can be classified into three types; (1) products formed by oxidative dealkylation of the N-propyl groups and reduction of nitro groups and a combination of both reactions, (2) cyclization products in the form of benzimidazoles, and (3) dimeric condensation products in the form of azo and azoxy derivatives. In addition, some photoproducts were not identified.

The identities of the photoproducts in investigated media were determined either by matching their mass spectra with the mass of trifluralin photoproducts and metabolites which are available in the literature while some were identified by GC-MS library search and the rest of them deduced by following their mass spectra pattern.

The mass spectra, chemical name and structure formula of trifluralin (Fig.3.5) and its photoproducts in n-hexane, methanol, and distilled water are given in Figures 3.6, 3.7, and 3.8 respectively while the major fragmentation of their molecular ions are presented in Tables 3.2.

Fig.3.5 Mass spectrum of trifluralin.

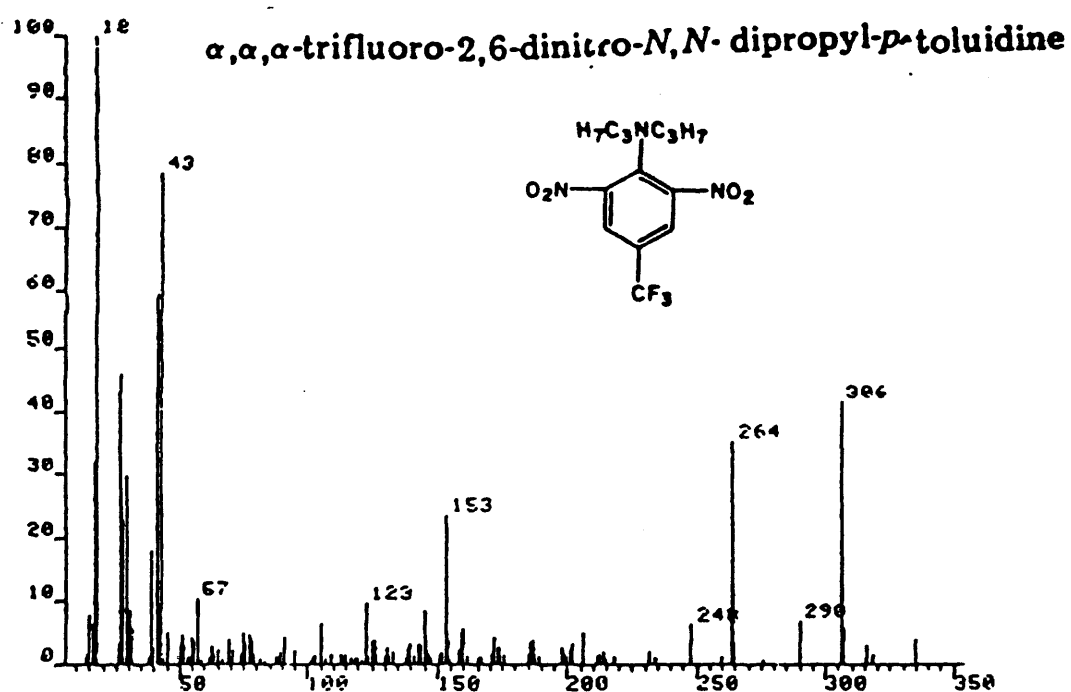
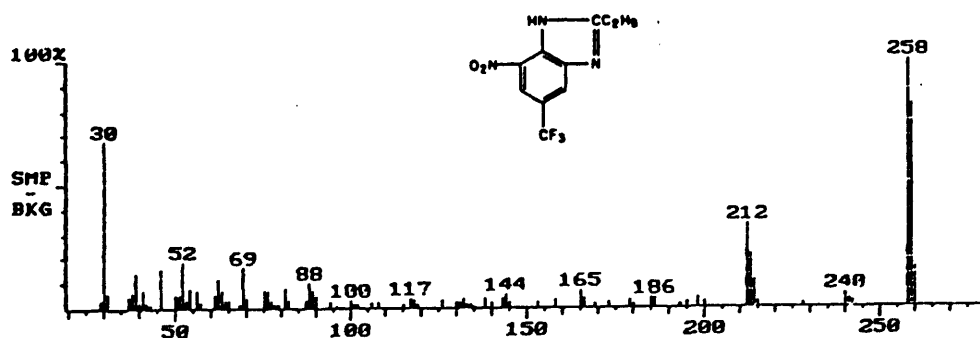


Fig.3.6 Mass spectra of trifluralin photoproducts in n-hexane.

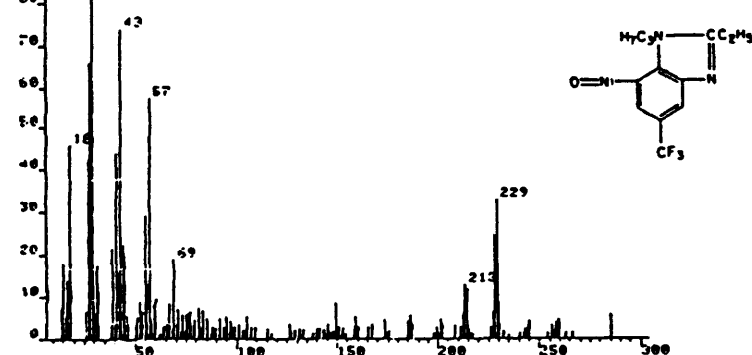
H1

2-ethyl-7-nitro-5-(trifluoromethyl)-benzimidazole



H2

2-ethyl-7-nitroso-1-propyl-5-(trifluoromethyl) benzimidazole



H3

2-ethyl-7-nitro-1-propyl-5-(trifluoromethyl)-benzimidazole

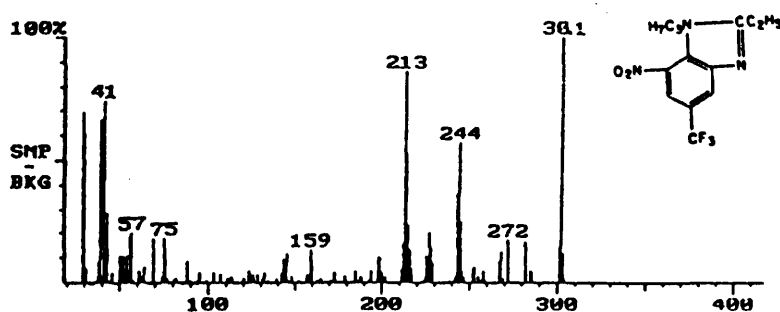
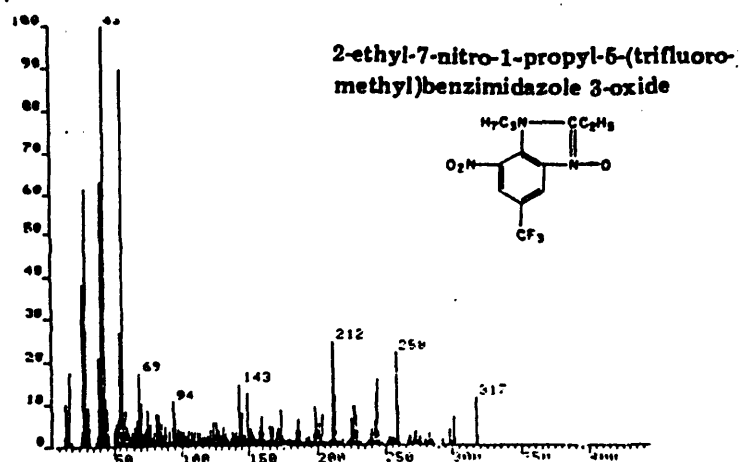
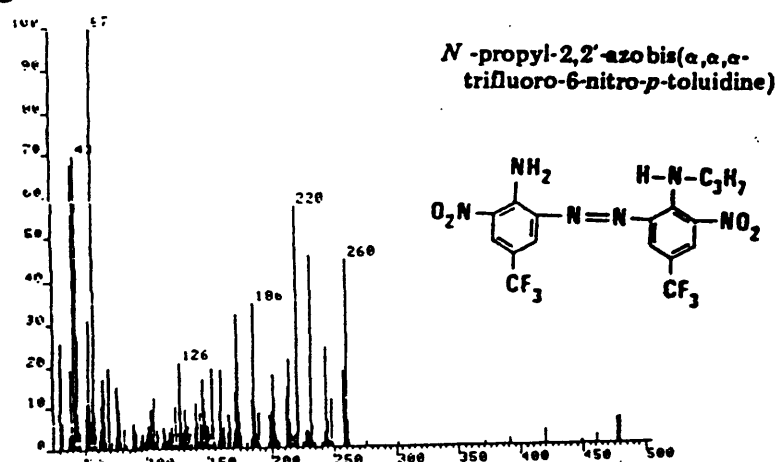


Fig.3.6 Cont.

H4



H5



H6

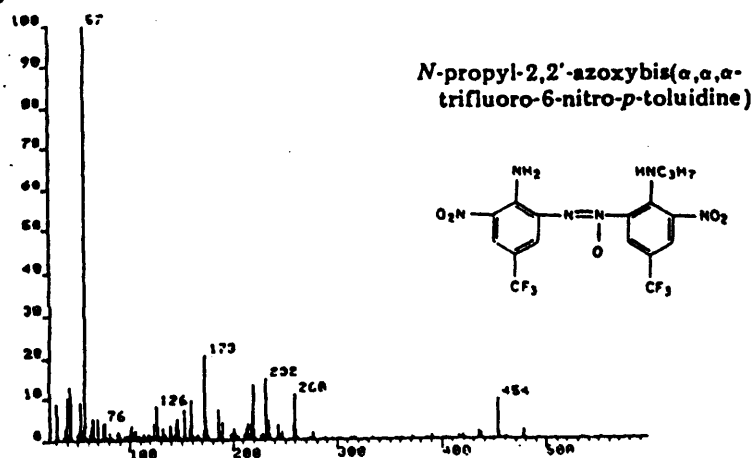
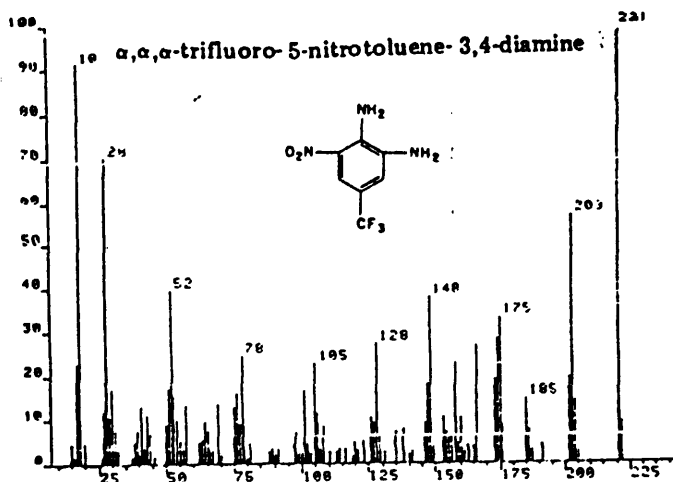
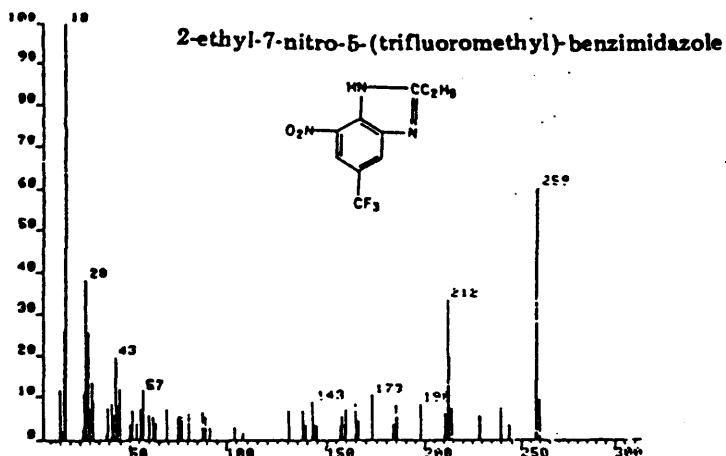


Fig.3.7 Mass spectra of trifluralin photoproducts in methanol.

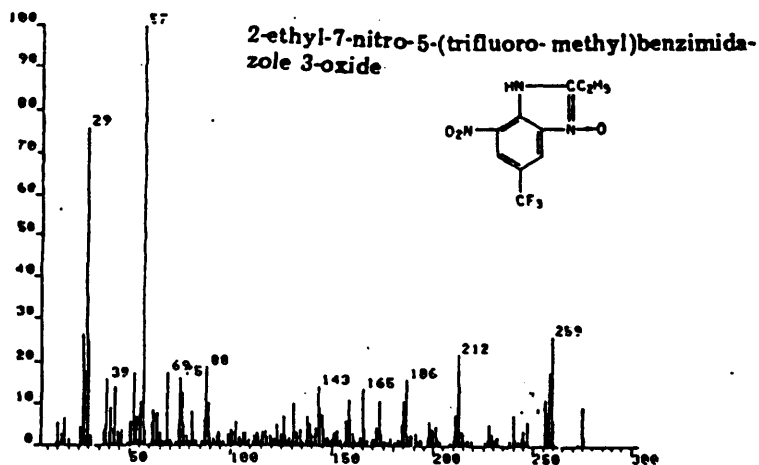
M1



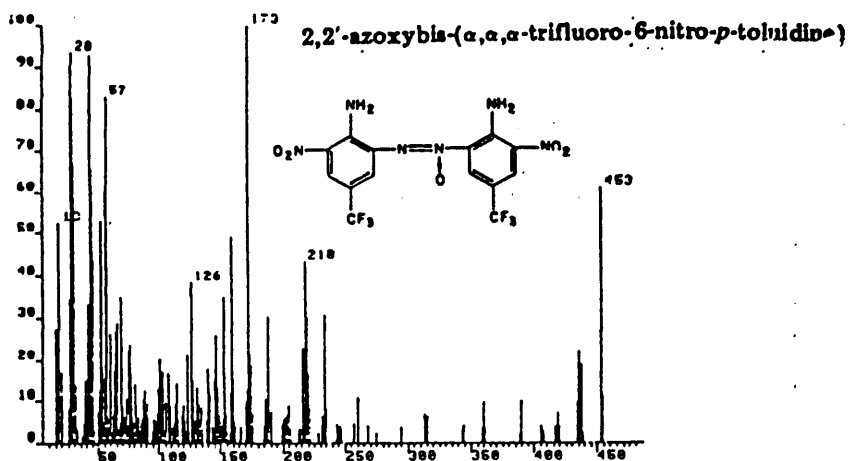
M2



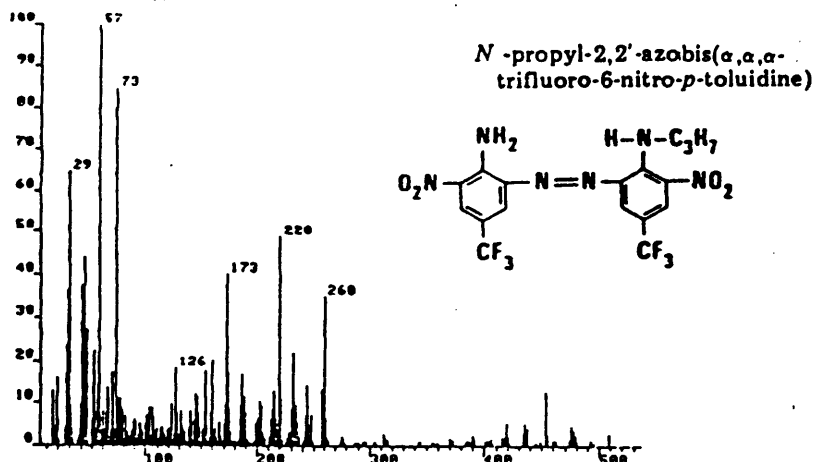
M3



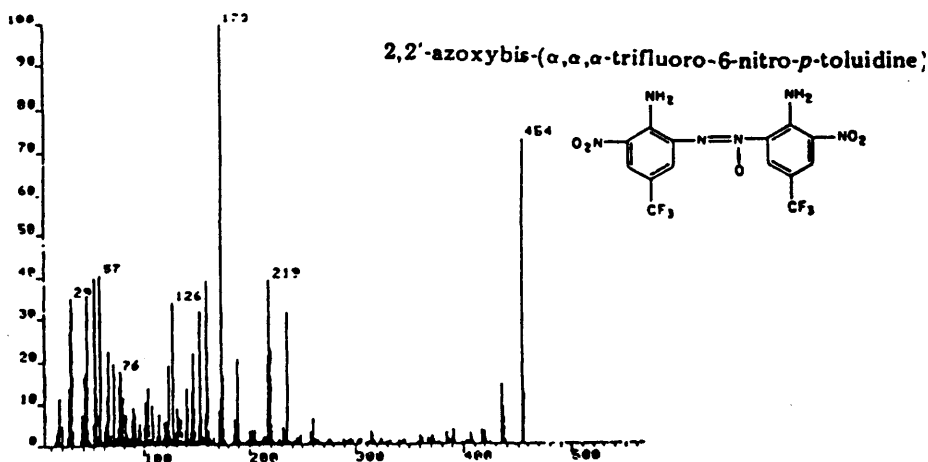
M4



M5



M6



M7

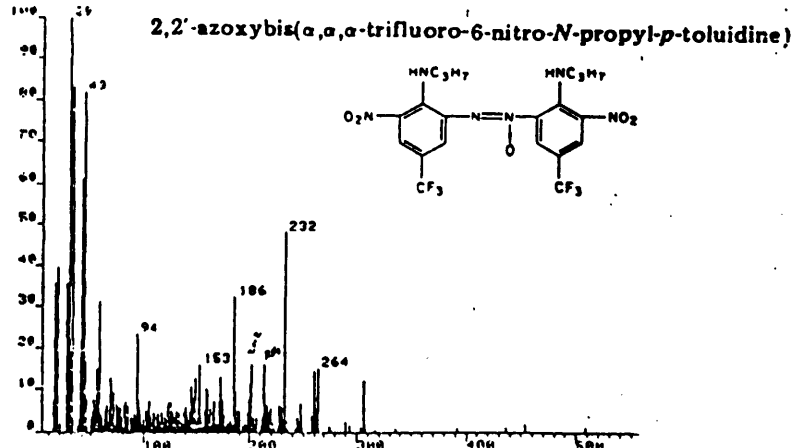
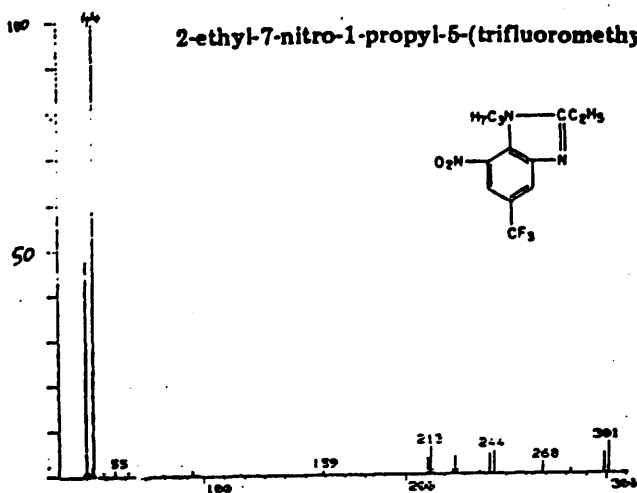
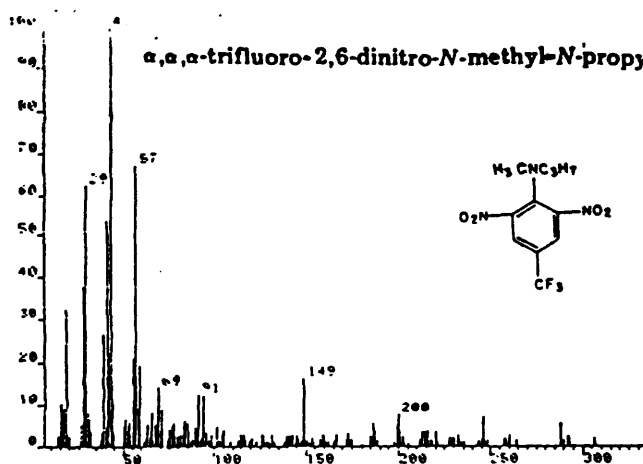


Fig.3.8 Mass spectra of trifluralin photoproducts in distilled water.

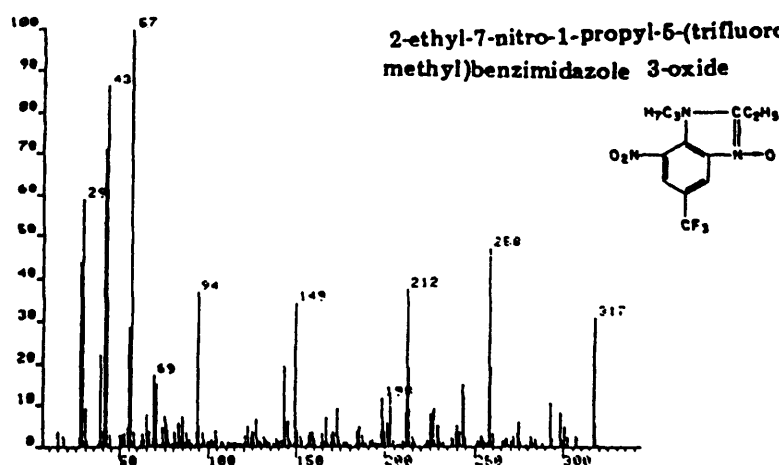
W1 2-ethyl-7-nitro-1-propyl-5-(trifluoromethyl) benzimidazole



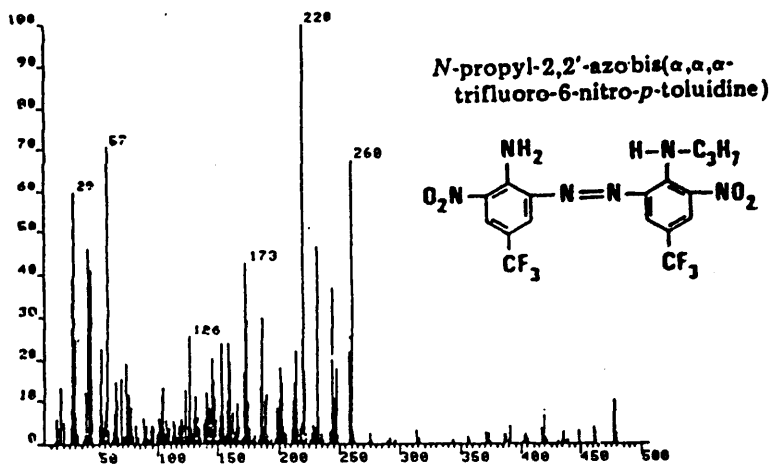
W2 α,α,α -trifluoro-2,6-dinitro-N-methyl-N-propyl-p-toluidine



W3 2-ethyl-7-nitro-1-propyl-5-(trifluoromethyl)benzimidazole 3-oxide



W4



W5

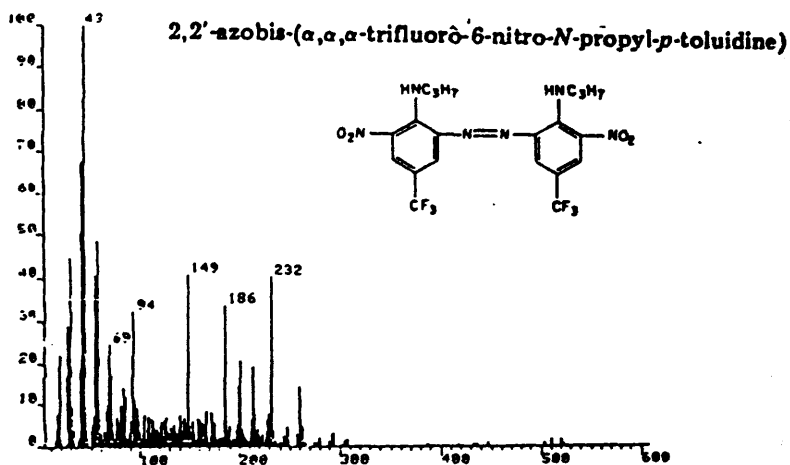


Table 3.2 Molecular ion of the trifluralin photoproducts and their major fragments in n-hexane [H], methanol [M], and distilled water [W].

Code	m/e (parent)	Major fragments
H1, M2	259	258, 213, 212, 185, 173.
H2	285*	256, 242, 229, 214, 199.
H3, W1	301	272, 258, 244, 229, 213.
H4, W3	317	301, 258, 244, 212, 198.
H5, M5, W4	480	260, 220, 232, 186, 174.
H6, M6	496	479, 477, 454, 276, 260, 258, 248, 244, 232, 186.
M1	221*	205, 203, 175, 173, 158.
M3	275	259, 247, 229, 228.
M4	454	235, 219, 205, 189, 173, 159.
M7	538	519, 509, 290, 276, 260, 258, 248, 232, 186.
W2	307*	293, 264, 235, 167, 149, 121.
W5	522	503, 261, 260, 232, 216, 215, 214, 202, 186.

* = Proposed from the fragmentation pattern only.

Only one photoproduct resulted from didealkylation and mono nitro group reduction was found only in methanol. Its proposed chemical name was α,α,α -trifluoro-5-nitrotoluene-3,4-diamine [M1] with m/e of 221. The m/e of its fragments and their corresponding losses were

205(M-O or NH₂)⁺, 203(M-H₂O)⁺, 175(203-CN₂H or M-NO₂)⁺, 173(203-NO)⁺, and 158(173-NH₂)⁺. A similar compound was obtained from three absorbents (sea sand, sandy loam, and organic soil) by Golab et al., (1979). This compound has not been reported as a photoproduct in any available literature and its mass spectrum has not been reported either. The dealkylation of the propyl groups and the reduction of the nitro groups in trifluralin have been reported by many workers.

Many benzimidazole derivatives were found in all the investigated media. A photoproduct with m/e 259 was found in n-hexane [H1] and in methanol [M2], 2-ethyl-7-nitro-5-(trifluoromethyl) benzimidazole. The m/e of its fragments and their corresponding losses were 258(M-H)⁺, 213(M-NO₂)⁺, 212(M-HNO₂)⁺, and 185(213-C₂H₄)⁺.

Other benzimidazole derivatives were found as well, in methanol with m/e 275 [M3]. This compound was proposed to be 2-ethyl-7-nitro-5-(trifluoromethyl)benzimidazole 3-oxide. The major m/e of its fragments and their corresponding losses were 259(M-O)⁺, 247(M-C₂H₄)⁺, 228(M-HNO₂)⁺, and 229(M-NO₂)⁺. A product with m/e 301 [H3 and W1] was found in n-hexane and distilled water which was 2-ethyl-7-nitro-1-propyl-5-(trifluoromethyl)benzimidazole. The m/e of its major fragments and their corresponding losses were 272(M-C₂H₅)⁺, 258(M-C₃H₇)⁺, 244(M-C₃H₅O)⁺, 229(258-C₂H₅)⁺, and 213(229-O)⁺. A similar photoproduct to the compound found here with m/e 259 ([H1],[M2]) was identified by Crosby and Moilanen (1972) when they exposed the vapour phase of trifluralin to UV light. They suggested that the product resulted from the cyclization of the nitro group with the α-carbon of the propyl group of the monodealkylated product of trifluralin. In addition, Leitis (1973), Crosby and Leitis (1973) and Leitis and

Crosby (1974) found the same products ([H1], [H3], [M2], [M3], and [W1]) in water, aqueous methanol, and aqueous suspension with or without soil. The same compounds were also isolated from soil as trifluralin soil metabolites by Golab et al., (1979) in sufficient amounts for identification. The mass spectra of these products were discussed by Golab and Occolowitz (1979). The mass spectra obtained were compared with the published mass spectra. Furthermore, the identity of the photoproduct ([H1], [M2]) was confirmed by using GC-MS equipped with library search. Moilanen et al., (1975) found a similar photoproduct to the photoproduct ([H3], [W1]) under anaerobic photolysis and they stated that the cyclization occurs only under anaerobic conditions.

A photoproduct with m/e 285 was found in n-hexane [H2], the proposed chemical name of which was 2-ethyl-7-nitroso-1-propyl-5-(trifluoro-methyl)-benzimidazole. The m/e of its major fragments and their corresponding losses were $256(M-C_2H_5)^+$, $242(M-C_3H_7)^+$, $214(242-C_2H_5)^+$, $229(242-CH)^+$, and $199(229-NO)^+$. This product was not reported in the available literature but there is a possibility of converting the nitro group to a nitroso group. This possibility was reported by McMahon (1966), when he exposed α,α,α -trifluoro-2,6-dinitro-N-methyl-p-toluidine in n-heptane bubbled with nitrogen to a UV source for 3 h which resulted in the formation of a product with the 2-nitro group converted to a 2-nitroso group. In addition, Plimmer and Klingebiel (1974) found a compound similar to that found by McMahon (1966) but from irradiation of another dinitroaniline compound, butralin.

A photoproduct with m/e 307 was found in the distilled water medium [W2]. It was proposed to be α,α,α -trifluoro-2,6-dinitro-N-

methyl-N-propyl-p-toluidine. The m/e of its fragments and their corresponding losses were $293(M-CH_2)^+$, $264(M-C_3H_7)^+$, $235(264-NCH_3)^+$, $167(235-CF_3+H)^+$, $149(167-H_2O)^+$, and $121(167-NO_2)^+$. This product has not been reported in the available literature and the deduction depended solely on the mass spectrum.

A photoproduct with m/e 317 was found in n-hexane [H4] and in distilled water [W3] as well. The suggested chemical name was 2-ethyl-7-nitro-1-propyl-5-(trifluoromethyl)benzimidazole 3-oxide. The m/e of its fragments and their corresponding losses were $301(M-O)^+$, $258(301-C_3H_7)^+$, $244(301-C_3H_5O)^+$, $212(258-NO_2)^+$, and $198(212-N)^+$. The same compound was reported by Leitis and Crosby (1974) as a precursor photoproduct while Golab et al., (1979) reported that the same compound resulted from the conversion of the precursor compound (α, α, α -trifluoro-2'-hydroxyamino-6'-N-propyl-p-propionotoluidide) on the TLC or in organic solvents and they confirmed its identity by TLC, GLC, MS and IR. In addition, Golab et al., (1979) determined the compound, 2-ethyl-2,3-dihydroxy-7-nitro-1-propyl-5(trifluoromethyl)benzimidazole which has been reported many times previously in the literature as a precursor to 2-ethyl-7-nitro-1-propyl-5-(trifluoromethyl)benzimidazole 3-oxide to be in error. However, Seiber et al., (1975) found the same product as a photoproduct of trifluralin in the vapour phase.

Five dimers such as azo or azoxy were found as photoproducts of trifluralin in investigated media.

The first with an m/e of 454 found in methanol [M4], was 2,2'-azoxybis(α, α, α -trifluoro-6-nitro-p-toluidine). The m/e of its fragments and their corresponding losses were 235(azoxy nitrogens fission)

ion)⁺, 205(235-NO)⁺, 189(205-NH₂)⁺, 173(219-NO₂)⁺, and 159(173-N)⁺. The same compound was isolated as a soil metabolite in insufficient amount for mass spectral identification but its nature was tentatively established by direct comparison with a model compound using various chromatographic methods (Golab et al., 1979). The mass spectrum obtained was compared with the discussed mass spectrum of the same compound found by Golab and Occolowitz, (1979). Leitis (1973) also found the same compound as a photoproduct when he irradiated trifluralin by sunlight in a water suspension at pH 5.5. He confirmed its identity by many methods.

The second dimer was found in all the investigated media, n-hexane [H5], methanol [M5], and distilled water [W4] as N-propyl-2,2'-azobis(α,α,α -trifluoro-6-nitro-p-toluidine). The major fragments were 260 and 220 due to the cleavage between the azo nitrogens and rearrangement of a hydrogen atom while the rest of the fragments were 232(260-C₂H₅+H)⁺, 186(232-NO₂)⁺, and 174(220-NO₂)⁺. The same compound was found by Sullivan et al., (1980) as a photoproduct of trifluralin in benzene and they discussed its mass spectrum for the first time. The mass spectrum gave the same pattern as that obtained in this work.

The third dimer was found in n-hexane medium [H6] and in methanol [M6] with an m/e 496, as N-propyl-2,2'-azoxybis(α,α,α -trifluoro-6-nitro-p-toluidine). Two isomers of this compound were isolated as trifluralin soil metabolites by Golab et al., (1979). Golab and Occolowitz, (1979) illustrated their mass spectra and distinguished between their structures. The molecular ion was of such low relative intensity that it could be easily hidden among peaks due to impurities in samples isolated from soil. The same thing was found

here, the molecular ion was not clear but the mass spectrum pattern was similar to that found by Golab and Occolowitz, (1979). The m/e, its fragments and the corresponding losses were 479(M-OH)⁺, 477(M-F)⁺, 454(M-C₃H₆)⁺, 276 and 220(fission of azoxy nitrogens with hydrogen transfer to the side has no oxygen)⁺, 260(276-O)⁺, 258(276-H₂O)⁺, 248(276-C₂H₄)⁺, 244(260-CH₄)⁺, 232(260-C₂H₄)⁺, and 186(232-NO₂)⁺. Sullivan et al., (1980) found the same compound as a photoproduct of trifluralin and they confirmed the structure by IR, NMR, and mass spectrometry. They reported also that the molecular ion was not always observed but could be detected in some spectra. The m/e of major fragments 260, 220, and 276 were reported and a small peak at m/e 276 indicated that the azoxy oxygen is located on the nitrogen attached to the same ring as the N-propyl group.

The fourth dimer found in distilled water medium [W5] with m/e 522, was 2,2'-azobis(α,α,α -trifluoro-6-nitro-N-propyl-p-toluidine). The m/e of its fragments and their corresponding losses were 503(M-F)⁺, 262, 261, and 260(fission of azo nitrogens and rearrangement of hydrogen atom)⁺, 232 or 231(260-C₂H₄ or C₂H₅)⁺, 216(232-NH₂)⁺, 215 or 214(261-NO₂ or with hydrogen atom rearrangement)⁺, 202(216-CH)⁺, and 186(232-NO₂)⁺. Sullivan et al., (1980) found the same compound as a photoproduct after irradiation of 25 g of trifluralin. They confirmed the identity of the photoproduct by comparing its mass spectrum with that published by Golab and Occolowitz, (1979) for the compound which they isolated from soil as a trifluralin soil metabolite. The mass spectrum obtained in this work gave the same pattern.

The fifth dimer with m/e 538 found in methanol medium [M7], was 2,2'-azoxybis(α,α,α -trifluoro-6-nitro-N-propyl-p-toluidine). The m/e

of its fragments and their corresponding losses were $519(\text{M-F})^+$, $509(\text{M-C}_2\text{H}_5)^+$, 290 and 248(fission of azoxy nitrogen-carbon bond with hydrogen rearrangement) $^+$, 276 and 260(fission between the azoxy nitrogens) $^+$, $258(290-\text{O}_2)^+$, $232(248-\text{O})^+$, and $186(232-\text{NO}_2)^+$. Sullivan et al., (1980) found the same compound as a photoproduct of trifluralin. Its mass spectrum pattern was similar to that found by Golab and Occolowitz (1979).

In addition to the twelve trifluralin photoproducts which were found in the different media in this work, there were two unidentified photoproducts with m/e 514 and 554, which are most likely dimers. Furthermore, there were many isolated bands on the TLC from which it very hard to get very clear mass spectra.

The structural deductions for the photoproducts [M1] (m/e 221), [H2] (m/e 285), [W2] (m/e 307) revealed that this was the first time such trifluralin photoproducts had been identified. The point should also be made that there is no readily available literature covering these products produced photochemically.

AN INTRODUCTION TO POTATO SPROUT SUPPRESSANTS

This chapter is a general background to the second part of this thesis which deals with an alternative use of the well known herbicide, trifluralin as a potato sprout suppressant. Some background to potato storage is given as a preliminary to the study.

4.1 The potato crop

The potato crop originated in the Andes region of Southern Peru and Northern Bolivia. The potato was presumably cultivated in South America for many centuries previous to 400 B.C. It was brought to Europe by the Spaniards at the end of the Sixteenth century A.D. Further introductions of potatoes from S. America have been made in more recent times, particularly after the disastrous blight epidemic of the 1840's (Howard, 1972). There was widespread opposition to the uptake of potatoes, frequently it seems because this crop was not mentioned in the Bible. In Russia, potatoes were referred to as "Devil's apples", while in France they were considered fit only for animals and poor people. Sweden was particularly slow in adopting them (Nash, 1978).

Nowadays potato (Solanum tuberosum L.) is a mainly European crop with the USSR as a major grower. The potato, as a staple dietary item, is an important source of carbohydrate in many countries. For instance, the human consumption in Britain alone is about 110 kg per

person per year (Anon. 1988).

In the U.K. seed potatoes are planted out at the end of April and are harvested late September onwards. The expected potato production in the U.K. is about 6-7 million tonnes per year (Anon., 1985a; Anon., 1985b).

The relative importance of the nutritive value of potatoes compared with other foods has never been fully appreciated. It is rich in vitamin C and its protein possesses a very high Biological Value (Nash, 1978).

4.2 Storage of potato

After harvest, potatoes have to be stored for a shorter or a longer period in order to supply the market throughout the year for direct human consumption as well as for the processing industry.

In early nineteenth century, the normal practice was to store potatoes in clamps, pits or pies, or in cellars. Only since the middle of the twentieth century has the low-cost clamp given way to widespread storage in buildings (Nash, 1978).

The techniques of potato storage have changed during the last 25 years. Outdoor clamp storage has almost disappeared and the vast majority of potatoes are now stored in buildings many of which have been specially designed for this purpose. Bulk storage is by far the most popular technique, although bin and box storage are now becoming

more common. In Scotland storage of seed in 0.5 or 1.0 tonne boxes is now widespread especially amongst the merchant-growers, as numerous cultivars can be conveniently handled in the same store by this method (Dalziel, 1978).

In bulk storage, the potatoes are stored in adapted stores with walls thickened to withstand the pressure generated by the potatoes particularly as they are loaded into store. Fluctuations in temperature can be corrected by ventilation, either internal recirculation or bringing in an amount of outside air dependent on the temperature required.

In box storage, the potatoes are loaded into 0.5 or 1.0 tonne wooden boxes which are stored in stacks up to 5 or 6 high. Despite the initial outlay on wooden boxes which is offset to some extent by the removal of the need to strengthen walls, this method of storage originally used mainly for seed growers, has proved popular among processors. The control of temperature in this storage system is better than that for bulk stores. The control of the material is much better and boxes from individual growers can be identified (Boyd, 1988).

The new stringent requirements of the processing industries throughout the year have also led to modifications in storage systems. Potatoes must be able to be stored from harvest through to the following July, in order to meet demand throughout the year for both raw and processed potatoes.

Depending on the scale of the operation, the tubers are stored in small stores or transported to large centralised stores. Because

of damage caused by harvesting and grading procedures, tubers are allowed to wound heal for several weeks. This period is known as the wound healing or curing time. Most sprout suppressant chemicals affect wound healing adversely and for this reason tubers are treated with these chemicals after wound healing has occurred or applied in special slow release formulations to ensure adequate time for wound healing (Boyd, 1988).

Potato tubers are living organisms containing a high percentage of water and during their post-harvest life they are subject to weight losses and decrease in quality due to respiration, changes in chemical composition, sprouting, disease and evaporation of water.

The main factors which affect tuber quality are sprouting following break of dormancy and developing bacterial (soft rots, black leg, and brown rot, bacterial ring rot) or fungal diseases (dry rot, gangrene, pink rot, watery wound rot, and blight).

The aim of potato storage is to keep, in an economical manner, losses in quantity and in quality to the lowest possible level. It is possible today to keep potatoes in an adequate store with good management for a period as long as 10-12 month without excessive losses in weight and quality. In general, healthy, undamaged, mature potatoes with a well suberized skin, harvested under good weather conditions can be stored satisfactorily over this period (Hesen, 1981).

4.3 Sprouting

Length of dormancy period after harvest depends on many factors such as variety, climate during the growing season, infection, and storage temperature. The most important factors influencing the period of dormancy are the variety and the temperature of storage.

Sprouting normally does not start immediately after harvest and the dormant period lasts from several weeks to several months depending on the variety, growing conditions, damage, disease, physiological age of the tubers and storage conditions (Hesen, 1981).

The sprouting of potatoes might be controlled by their content of growth substances. This was an early suggestion but later it was suggested that dormancy results from the inhibition of bud growth by too high concentration of auxin. More recently, the role of gibberellins was recognized only as a part of a complex balance of factors (Burton, 1966).

Sprout growth causes excessive losses due to an increase in evaporation and respiration and moreover sprouted potatoes are more susceptible to disease (Hesen, 1981). In addition, Leonard (1988) stated that tuber sprouting can lead to tuber softening due to moisture loss, difficulties with the unloading and dressing of the potatoes, metabolic changes which can affect the quality of the potatoes, and development of internal sprouts.

For these reasons control of sprout growth during storage is very important and must be controlled.

4.4 Sprout control

Sprout growth can be achieved by any of the following : (1) storage temperature. (2) light. (3) irradiation. (4) natural sprout control. (5) chemical sprout suppressants.

4.4.1 Storage temperature

An increase in the rate of sprout growth will occur as the storage temperature is increased above 2°C, reaching an optimum at round 15-18°C. A further increase in temperature leads to reduction in the growth rate over an extended period, although initially sprout growth may be more rapid at 23-25°C (MacGee et al., 1986).

McKenzie (1989) and Leonard (1988) reviewed that storage of potatoes at 4°C reduces or stops sprouting, but can cause side effects such as increased reducing sugars and sweetening, and increased disease and damage (McKenzie, 1989). Reducing sugars make this type of sprout control impracticable for tubers which are to be processed into crisps as the product is usually unacceptably dark brown in colour.

The processing industry must, therefore, store potatoes at a temperature high enough to minimise low temperature sweetening and also low enough to minimise sprouting and water loss. In practice, a temperature of 7-8°C is considered optimal (Boyd, 1988).

4.4.2 Light

Potato sprouts grown in the light develop chlorophyll and are shorter and sturdier than those grown in the dark (Burton, 1966). He also reviewed many studies dealing with the effect of different light wavelengths on the sprouting of potato tubers. A very considerable reduction of sprout growth by blue, violet, red and infra-red radiation was observed compared with growth in darkness. Reduction of sprout elongation by exposure to yellow and green light was marked but not so great as it was on exposure to light of other wavelengths. The effect was dependent on the intensity of the radiation.

More recently McGee et al. (1987) using narrow-band width light sources, showed a peak of growth inhibition at 707 nm (in red region). The 400-500 nm (blue) had some inhibitory activity as well.

Light is used commercially during pre-sprouting of seed potatoes to produce strong sprouts to avoid mechanical damage during planting. In addition, natural light is gaining in widespread use for controlling sprout growth in the tropics in small scale. In Europe this method is known as chitting. The potatoes are exposed to the light on wooden trays in order to secure earlier growth. In tropical climates, the diffuse-daylight seed storage system is used to allow the seed potatoes to be in a plantable condition for 6-8 months between seasons (McGee et al., 1987).

4.4.3 Irradiation

Dormancy may be prolonged indefinitely by irradiating the tubers with Gamma-rays at 5,000-20,000 rads or electrons or X-rays. Informations on this topic is well reviewed by Burton (1966).

Leonard (1988) stated a possible mechanisms by which irradiation inhibits sprout growth. This speculation included, interference with nucleic acid synthesis in the meristematic region of sprouts, disturbance of the phosphorylation process, inhibition of the formation of the auxin, indoleacetic acid, and chromosomal changes in the cell of the meristematic tissue which prevent normal cell division and growth.

Irradiation for sprout control has many disadvantages such as increasing rots, an effect on wound healing, a change in taste, after-cooking blackening, residual radiation, increase in reducing sugars, and the ~~faers~~ ^{fact} that until this treatment inhibition is irreversible.

More recently Muir et al. (1987) confirmed that an initial increase in reducing sugars was shown to drop down to an acceptable level after 200 days of storage at 8°C. There is a positive relationship between irradiation doses and initial sugar levels.

The commercial viability of irradiation as a method depends on the cost of the radiation source required and the cost of transportation of potatoes to and from the source.

4.4.4 Natural sprout control

The volatile natural potato product, 1,4-dimethylnaphthalene (DMN) has sprout suppressant properties as demonstrated by a simple bioassay (Meigh et al., 1973). Beveridge et al. (1981) assessed twenty naturally produced volatile chemicals and found only two chemicals were effective at 100 mg kg⁻¹, compared with tecnazene at 120 mg kg⁻¹ in controlling sprout growth over twelve weeks. These two chemicals were benzothiazole and 1,4-dimethylnaphthalene.

Many other substituted naphthalenes were tested and found active as sprout suppressants (Stephen & Duncan, 1984).

O'Hagan et al. (1987) found that the dimethylnaphthalene analogues which were least successful as sprout suppressants also produced the smallest headspace concentration.

4.4.5 Chemical sprout suppressants

Dalziel (1978) carried out a survey of many chemicals used for sprout suppression, some of which are in commercial use while some have been used commercially and are now superceded and others which have never been tested commercially.

In the present time, there are four chemicals widely used as potato sprout suppressants. These chemicals are chlorpropham and its

unchlorinated analogue propham, tecnazene, and maleic hydrazide.

4.4.5.1 Chlorpropham and Propham

Chlorpropham, isopropyl N-(3-chlorophenyl)carbamate, was introduced as a potato sprout suppressant in 1950 by Marth and Schultz (1950) and then became the most widely used in North America and Europe.

Chlorpropham is a cell division inhibitor and thereby prevents sprout growth.

Usually, chlorpropham is applied at a rate of $10-20 \text{ mg kg}^{-1}$. The application is carried out as a thermal fog of chlorpropham mainly in a methanol formulation. Also the application may be carried out by using a solid formulation an approach not favoured in the UK.

Many problems are associated with using chlorpropham such as the prevention of wound healing (Leonard et al., 1986) so this chemical cannot be applied to the potatoes as they are loaded into the store. Also it can effect tuber components (Ponnampalam & Mondy, 1986), and by being absorbed onto wood and cement can inhibit the germination of stored seed crops for subsequent years. A skinspot blemish (McGee, 1984) and high residue levels $1-80 \text{ mg kg}^{-1}$ are not uncommon in unwashed whole tubers (Dalziel & Duncan, 1980). In addition it should be emphasized that chlorpropham cannot be used on seed potatoes.

Propham, isopropyl N-phenylcarbamate, is always used in a mixt-

ure with chlorpropham when applied to potatoes (approximately 1/5th) and is never used alone. The first use was in early 1950's and was reported by Rhodes et al., (1950).

Propham is similar to chlorpropham in its mode of action and the problems which are associated with its use.

4.4.5.2 Tecnazene

Tecnazene, 1,2,4,5-tetrachloro-3-nitrobenzene, is used as a sprout suppressant on ware and seed potatoes at a level of 135 mg kg⁻¹ although lower rates are often used on potatoes intended for processing as an initial treatment, prior to applying chlorpropham. The chlorinated nitrobenzenes have been known to inhibit potato sprouting since the 1940's (Brown, 1947). Its mode of action is not yet known.

It is formulated in many ways eg foggable liquids, granules and powders.

Tecnazene can be applied after harvest directly because it does not inhibit wound healing (Burton, 1966; Leonard et al., 1986). In recent years (Leonard, 1988), it has become common practice to control the sprouting early in the storage season with tecnazene, followed by applications of chlorpropham when needed throughout the storage period.

Leonard (1988) reported the disadvantages related to the use of tecnazene such as high cost, a question mark about its toxicity, its persistence as organochlorine compounds can be resistant to breakdown in the environment.

Tecnazene is the only commercially available sprout suppressant that may be used with any degree of confidence on seed potatoes and particularly in the past was widely used in Scotland (Daziel, 1978).

4.4.5.3 Maleic hydrazide

Maleic hydrazide, 6-hydroxy-3-(2H)-pyridazinone, has been used as a growth regulant for many years particularly in the USA on tobacco, onions, and as a potato sprout suppressant. One foliar treatment at a rate of 1.7 kg ha^{-1} is sufficient to retard sprouting until the end of the storage season (Burton, 1966). For optimum performance maleic hydrazide must be applied at flowering.

The main problems associated with using maleic hydrazide are the high residue in the tuber flesh (translocated compound), and its implications as a potential carcinogen. In addition, maleic hydrazide can not be used on seed potatoes.

The U.K. climate is unfavourable for efficient uptake and translocation of maleic hydrazide to the tubers, leading to insufficient for sprout inhibition (Corbett et al., 1984).

4.5 The case for using trifluralin as a sprout suppressant

Firstly an understanding of the properties which are essential for sprout inhibition. The essential properties of the famous commercial sprout suppressants (chlorpropham and propham) which enable them to act as potato sprout inhibitors in the store are their biological action (cell division disruption) and their physical character (volatility).

As mentioned above most sprout suppressant chemicals have applications in other fields of agriculture (herbicides, fungicides) and their sprout suppressant properties have been discovered later. However, to design a chemical specifically for sprout suppression is very costly, and ultimately could cost many millions. The dinitroaniline, trifluralin (α,α,α -trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine) has been used as a pre-emergence herbicide for the control of the germination of annual grass and broadleaf weeds since the early 1960's.

Probst and Tepe (1969) reviewed the early studies. They summarized the morphological and histological evidence which demonstrates the effect of trifluralin on plant-cell division.

Excellent morphological and histological descriptions of the influence of dinitroaniline herbicides on root meristem tissue have been published by Bayer et al. (1967). They found that trifluralin disrupted the mitotic process. Not one type of mitotic figure prevailed. Mitotic activity was not affected in all of the cells, some of which appeared to be undergoing a perfectly normal mitosis. In addi-

tion, Parka and Soper (1977) summarized the research that has been conducted to elucidate the mechanism of action of the dinitroaniline herbicides. These herbicides do not directly inhibit the germination of seed. Inhibition of lateral root development is the most characteristic growth response. Swelling of the root tip is a universally recognized morphological effect caused by these compounds. Enzyme activity does not appear to be greatly inhibited by the dinitroaniline herbicides.

Herbicides influence cell division in two ways. In the first, mitotic cells are totally absent, thus the overall effect is an inhibition of cell division. In the second, mitotic cells are present after herbicide treatment, but they are abnormal, thus cell division is disrupted (Hess, 1983). Hess also reported the differentiation in the inhibition of cell division by trifluralin, propham and chlorpropham. Trifluralin prevented the spindle formation while propham and chlorpropham disrupted the the spindle function. In other studies he also reported that trifluralin caused a disruption of cell division because of an inhibition of spindle microtubule formation during prophase (Bartels & Hilton, 1973; Hess & Bayer, 1974) while Talbert (1965) suggested that trifluralin interfered with the normal function of the spindle. After 24 h of the treatment numerous polynucleate cells were present and at lower concentrations, growth and cell division resumed after 24 h. He calculated also that trifluralin acts as a mitotic poison. However, Hess (1989) reported that the stages of mitosis that require the function of a spindle apparatus (metaphase, anaphase, and telophase) become absent in dinitroaniline-treated meristems, whereas the stage that does not require the active participation of the spindle (prophase) is not altered. This suggests

that the influence of dinitroaniline herbicides on mitosis is related to the spindle apparatus.

Upadhyaya and Nooden (1977) summarized the similarities between effects of colchicine and dinitroaniline herbicides as follows: inhibition of root elongation, induction of swelling in the elongation zone, a lag time in their effects, disruption of mitosis, change in the polarity of cell enlargement, thin walls in the swollen cells, lack of inhibition of cell enlargement at physiologically active concentrations, and disappearance of microtubules.

Hess and Bayer (1977) found that trifluralin binds to tubulin protein isolated from the flagella of the alga *Chlamydomonas*. They suggested the observed trifluralin binding might prevent tubulin polymerization into microtubules, thus explaining the absence of microtubules in mitotic cells. More recently, Appleby and Valverde (1989) summarized much literature in this field, which demonstrated that dinitroaniline herbicides injure plants by binding to tubulin, a dimer protein in the cell that polymerizes to form microtubules which form the spindle fiber, which enable chromosomes to separate during cell division. Microtubules also are responsible for orienting cell wall microfibrils in such a way that they prevent lateral enlargement of cells. This leads to one of the common symptoms-spherical cells instead of rectangular ones.

Hepler and Jackson (1969) reported that prophan changed the microtubules from normal parallel alignment at metaphase and anaphase to radial arrays. This orientation has been termed a multipole spindle apparatus.

It is known that the polymerization of microtubules is affected by calcium (Ca^{2+}), thus if the concentration of Ca^{2+} increases, depolymerization of the microtubules will occur. Plant mitochondrial experiments by Hertel et al. (1980) with trifluralin, propham, and chlorpropham showed that these herbicides diminished Ca^{2+} uptake. Thus if the level of cytoplasmic Ca^{2+} is raised the organization of microtubules could be inhibited.

Hess (1989) reviewed another characteristic effect of dinitroaniline, viz swelling of the cell-elongation zone of the root-tip area which results from aberrant cell enlargement.

Propham acts directly on the microtubule organizing centre so propham disturbs the orientation of microtubules arising from this centre. Thus, the N-phenylcarbamates do not cause spindle absence as do the dinitroanilines, they cause the spindle function to be aberrant. This information is reviewed by Hess (1989). He also reviewed other studies, which showed that high concentrations of propham and chlorpropham inhibit mitotic entry. In addition to the spindle effects, various types of chromosome abnormalities are caused by N-phenylcarbamate herbicides.

From the above review, it is very clear that the mode of action of trifluralin, chlorpropham, and propham on the plant cells are same as cell division inhibitors inspite of the fact that they exhibit different mechanisms to inhibit the cell division process.

The other property which is essential in the practical use of

sprout suppressant in commercial potato stores the volatility. Chlorpropham and tecnazene are volatile compounds and when transported in the vapour phase they can suppress sprout growth (Boyd & Duncan, 1986).

Phytotoxicity of trifluralin and other dinitroaniline herbicides by vapour phase was reported in the literature. Swann and Behrens (1972) determined the phytotoxic potential of trifluralin vapour. They found that, the root and shoot growth of two millet species was inhibited by trifluralin vapour arising from soil treated with 5 ppm of trifluralin. Negi and Funderburk (1968) reported that corn seedlings exposed to vapour from trifluralin solutions exhibit typical trifluralin injury symptoms.

The physical and some biological properties of the commercial sprout suppressants and trifluralin are presented in Table 4.1. More information about the volatility of trifluralin can be found in Chapter 2.

Due to the presence of the essential characters (cell division inhibition and volatility) required by commercial sprout suppressants in trifluralin the possibility was considered of investigating the use of trifluralin as a potato sprout suppressant.

Table 4.1 Some physical and biological properties of sprout suppressant chemicals and trifluralin.

	Trifluralin	CIPC	IPC	TCNB	MH
Molecular weight	335.28	213.67	179.22	260.96	112.10
Vapour pressure (Pa) at 25°C	0.0137	0.039	-	0.06	not volatile
Solubility in water(ppm) at 25°C	0.5	89	25-250		6
Melting point (°C)	48.5-49	41	87-88	99	296
Boiling point (°C)	96-97	247	sublimes at room temperature.	304 with decomposition.	-
Mode of action	mitosis inhibitor.	mitosis inhibitor.	mitosis inhibitor.	unknown	mitosis inhibitor.
Toxicity, LD ₅₀ rat, oral (mg kg ⁻¹)	>10,000	5,000-7,500	5,000		>5,000
CIPC	Chlorpropham				
IPC	Propham				
MH	Maleic hydrazide				
LD ₅₀	Lethal Dose of 50% of test population				
Pa	Pascal				

4.6 Toxicology

As trifluralin will be applied directly on human food, in its proposed alternative use as a potato sprout suppressant, more care must be taken to investigate many aspects concerning human safety. These are toxicity, metabolism in plants and animals, and the residue level of trifluralin which reaches the consumers. It is difficult to judge the safety use of any chemical in this field since the available data have been derived from animal experiments which are not necessarily directly applicable to human beings.

Degradation of dinitroaniline herbicides including trifluralin in plants and animals has been discussed in Sections 1.6 and 1.7 respectively of Chapter 1. Trifluralin is degradable and metabolize into water-soluble metabolites in higher plants which mainly resulted from dealkylation of propyl groups, and reduction of nitro groups. The conversion of the trifluoromethyl group to a carboxylic acid is also a possibility.

Trifluralin apparently is metabolized in animals by reduction of nitro groups and removal of the N-propyl groups while other possibility which could occur in the environment such as cyclization, condensation to form azo, azoxy derivatives and altering the trifluoromethyl group to a carboxylic acid have not been extensively studied.

Probst et al. (1976) reported that extensive toxicological data obtained on trifluralin indicate that it constitutes no hazard to man or animals when used as directed. The acute oral LD₅₀ of trifluralin for adult rats is greater than 10 g kg⁻¹. Exposure of rats to a mist

containing 2.8 mg l^{-1} caused no adverse effects. No skin irritation was observed in rabbits treated dermally with 2.5 g kg^{-1} . Rats were fed 2000 ppm of trifluralin in their diet for a two-year period without adverse effect and with no change in reproduction or fertility through three generations. Trifluralin was given daily to dogs at 1000 ppm in their diet for two years without adverse effect.

The LC_{50} of trifluralin as an emulsifiable concentrate in static fish ponds is 0.058, 0.094, and 0.560 ppm for bluegills, fathead minnows, and goldfish, respectively. If trifluralin is first sprayed on soil then added to static water, the LC_{50} value for bluegills is 2.8 ppm on Princeton fine sand and 13.2 ppm on Brookston silty clay loam.

Worth (1968) abstracted data obtained with benefin and trifluralin in the rat, dog, rabbit, chicken, and fish which indicated these compounds were not hazardous to any species except fish. Studies in animals with metabolites from both compounds show these likewise show similar safety. Results of two-year feeding studies to rats and dogs, of multiple generation breeding studies in rats, teratology experiments in rabbits, and information from several ancillary experiments, all demonstrated no effect.

Generally the reported values for acute oral toxicity, dermal, and inhalation toxicities reveal little toxicity to mammalian species. The notable point regarding toxicity is that related to fish but trifluralin exhibits low water solubility and a strong adsorption to the soil.

Mammalian toxicity of trifluralin is low but toxic by-products of manufacture such as nitrosamines (most likely carcinogenic in man) have been known to occur in some formulations (Cohen et al., 1978; Worthing et al., 1982). Ross et al. (1977) reported N-nitroso-dipropylamine present as an impurity in a formulation of trifluralin at the 154 ppm level. Subsequent studies by other laboratories showed that their nitrosamine contamination was present in all dimnitroaniline-based herbicides. The manufacturers were able to reduce this impurity from 154 ppm to 18 ppm. More recent data have shown that the level has now been successfully reduced to below 0.5 ppm (Fine et al., 1980).

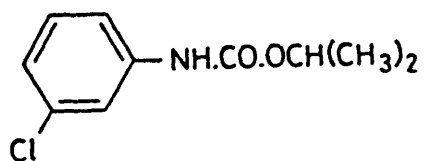
Yoon et al. (1985) described the results of chemical mutagenicity tests in Drosophila melanogaster for 45 chemical compounds, four of which were equivocal. Among these four were maleic hydrazide and trifluralin. However, trifluralin gave equivocal results in the feeding experiments and negative results after injection. They also reviewed other studies, where trifluralin gave negative results after larval and adult feeding.

Heck et al. (1977) studied the distribution and persistence of trifluralin in rats following injection or chronic oral administration. Following injection of 500 $\mu\text{g kg}^{-1}$ of trifluralin, trifluralin was detected at high concentrations in fat and at lower concentrations in liver. Trifluralin was not present at detectable levels in the plasma samples of most of the animals. Trace amounts were found in the 24-h urine collections of rats sacrificed 1 day post injection. While following chronic oral feedings of trifluralin at dose levels of 20, 100, and 500 $\mu\text{g kg}^{-1}$ daily for 21 days, trifluralin was detected

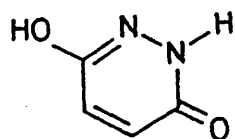
at low concentrations in fat in essentially all of the animals and in ^afeces only at the highest dosage. Many of the urine samples at the 500 ug kg⁻¹ dosage level appeared to contain trace amounts of trifluralin. Trifluralin was not found in liver, and its apparent presence in plasma at low concentration in a few samples may be erroneous. They explained that the oral route of administration evidently results in relatively little systemic absorption of the unchanged trifluralin. Also they reviewed that trifluralin is poorly absorbed from and extensively metabolized within the gut, presumably by microorganisms.

In conclusion the toxicity of trifluralin, in particularly if trifluralin will be added directly to the foodstuff does need more investigation.

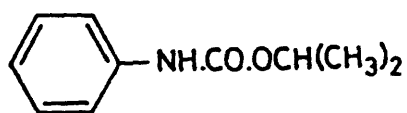
Fig.4.1 Trifluralin and the commercial potato sprout suppressant chemicals.



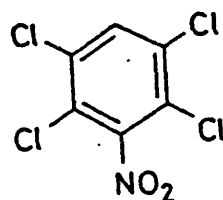
Chlorpropham



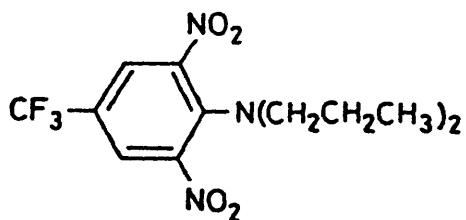
Maleic hydrazide



Propham



Tecnazene



Trifluralin

AN ASSESSMENT OF TRIFLURALIN FOR POTATO SPROUT SUPPRESSANT

5.1 Introduction

Due to the simillarity to the commercial potato sprout suppressants, propham and chlorpropham, with regard to mode of action (mitotic inhibitor) and volatility which are essential characters for commercial sprout inhibition (Chapter 4, Section 4.5), an investigation was carried out to investigate the possibility of using trifluralin as a potato sprout suppressant in this Chapter.

This Chapter involves many studies to check the possible ability of trifluralin as a potato sprout growth inhibitor. These studies were 1- a preliminary assessment of the ability of trifluralin to inhibit potato sprout growth followed by 2- an assessment of different levels of trifluralin to find the lowest effective level and 3- an analytical method for analysing the residues of trifluralin in potato tubers.

5.2 Experimental

5.2.1 Trifluralin preparation

Trifluralin was recovered according to the procedure of Holzer et al. (1963) from an emulsifiable concentrated formulation (Tristar, Pan Britannica Industries Ltd, England) which contained 480 g l^{-1} trifluralin active ingredient. The recovered trifluralin was checked for purity by infrared, mass spectrometry and melting point compared with standard trifluralin (99%) purchased from Alltech Associates/Applied Science, England. The purity of the recovered trifluralin was 97%.

5.2.2 Preparation of dust formulation

Before the preparation of dust formulation of trifluralin, the stability of trifluralin on the solid carrier material had to be tested, neutral aluminium oxide was used. 10 g of neutral aluminium oxide (Brockman grade 1, BDH Chemicals Ltd, Poole, England) were spiked with 2 cm^3 of 1000 ug cm^{-3} trifluralin in hexane, in a 150 cm^3 glass bottle, then 1 cm^3 of distilled water was added. The bottle was sealed, using a teflon seal and covered with aluminium foil to avoid exposure to the light. The bottle contents were mixed well by shaking for 1 h, using an end-over-end shaker. An appropriate control treatment was carried out, using alumina alone or alumina plus distilled water. All treatments were carried out in duplicate, then they were incubated for 6 days at 35°C , using a water bath. After 6 days of incubation, trifluralin was extracted with two 25 cm^3 portions of

hexane-acetone (3:1) by shaking for 10 min. The combined extract was evaporated, using a vacuum rotary evaporator at 35°C, then the residues were dissolved in hexane and made up to 25 cm³. A gas chromatography equipped with flame ionization detector was used for analysis. Trifluralin was stable under these conditions.

The trifluralin dust formulation for the preliminary assessment treatment was prepared as follows, 2 g active ingredient (a.i.) trifluralin in 50 cm³ of n-hexane (Glass distilled grade, Rathburn Chemical Ltd, Scotland) was added to 100 g of neutral aluminium oxide in a 500 cm³ round bottom flask, then the flask contents were mixed well by hand shaking for 30 min. The hexane was evaporated, using a vacuum rotary evaporator at 35°C then the dry alumina was mixed again by shaking for another 30 min before being homogenized. For the assessment of different levels of treatment the procedure mentioned above was followed with adding different amounts of trifluralin (1.5, 3.0, and 4.5 g a.i.) individually to 375 g of alumina in 1 l round bottom flask as required.

Chlorpropham dust formulation was prepared by following the same procedure as for the trifluralin dust formulation using 3 g a.i. of chlorpropham to 375 g of alumina.

The homogenization of the dust formulation was checked by analysing three 1 g samples which were taken randomly from the round bottom flask prior to the treatment of the potato tubers.

5.2.3 Potato treatment

1- Preliminary assessment treatments were carried out at one level of trifluralin, 50 mg kg^{-1} . 10 kg of freshly harvested and non injured potatoes of c v. Pentland Squire were placed in a cardboard box (38*31*15 cm). The boxes were kept at room temperature for two weeks to let wound healing take place. Then 25 g of the prepared trifluralin dust formulation were dusted over the potatoes in each box to give a treatment level of 50 mg kg^{-1} . Control treatment was treated with 25 g alumina containing no trifluralin. Chlorpropham was used as a reference compound. 25 g of the prepared chlorpropham dust formulation were dusted over potatoes in each of the chlorpropham treatment boxes to give a treatment level of 20 mg kg^{-1} this being the recommended rate for potato sprout control. Then the boxes were closed by lossely fitting lids. All treatments were carried out in three replicates. The boxes were then stored in a cold room at $10^{\circ}\text{C} \pm 1$ (Plate 5.1).

Plate 5.1 Treated potatoes stored in boxes at 10°C.



2- Assessment of different levels of treatment were carried out at three concentrations of trifluralin. These levels were 0, 10, 20, and 30 mg kg⁻¹. A reference treatment using chlorpropham at the recommended rate was included as well. In this assessment two potato cultivars were used, Maris Piper and Pentland Squire. The procedures of application and storage were the same as used in the preliminary assessment. All the treatments were replicated three times.

5.2.4 ^PSampling for residues analysis and sprout growth observation

1- In preliminary assessment, 3 tubers samples for trifluralin residues analysis were taken monthly for the first five months after treatment and the last sample was at the end of the assessment period (10 months). Each sample was taken randomly from each box.

The length of the longest sprout of 20 tubers of each replicate of all treatments were measured and the numbers of open eyes per tuber were counted as well at the same time as samples were taken for residues analysis.

2- In the assessment of different levels, 1 kg samples of potatoes for trifluralin residues analysis were taken after 3, 10, 18, 23, and 31 weeks of treatment. Each sample was taken randomly from each box.

The length of the longest sprout of 25 tubers of each replicate of all treatments were measured. This ^emeasur_ument was taken after 6, 20, and 31 weeks of treatment.

5.2.5 Growth test of trifluralin treated potato tubers

After three months of treatment 10 tubers from each replicate of the preliminary assessment were freely aerated at room temperature ($20^{\circ}\text{C} \pm 2$) for one month by placing the tubers on a tray. At the end of the airing period samples of three tubers from each replicate were taken for residue analysis.

After one month of airing two tubers from each replicate were planted in a pot 15 l in size containing a mixture of peat and sand at 1:1 ratio. The planted pots were placed in a growth room at $22-25^{\circ}\text{C}$ and fluorescent light for 24 h. Two non aerated tubers from each replicate of trifluralin treatment were also planted in the same way to see the effect of airing on the potato tuber growth. Two months after planting, the plants were cut 1 cm above the surface of soil and weighed.

5.2.6 Analytical technique

5.2.6.1 Sample preparation for residues analysis

The samples mentioned in Section 5.2.4, were kept in a deep freeze in sealed polyethylene bags until analysis.

1- In the case of preliminary assessment, the distribution of trifluralin residues was investigated within the potato tuber. The sample of three tubers was washed by tap water then left on a tissue paper to dry. Each tuber was peeled and the tuber flesh was divided into a 1 cm depth and a rest of the flesh, using a sharp knife. Each part was cut finely and combined to its corresponding and mixed. The knife was rinsed by acetone and new disposable gloves were used after every step to avoid any possible contamination between the three parts of the tuber. A sub-sample of 25 g finely cut was taken for residue analysis.

2- In the case of assessment of different levels study, the residues of trifluralin were determined in the peel and the rest of tuber (flesh). Sample of 1 kg was washed by tap water then left on tissue paper to dry. All the tubers of the sample were peeled using a peeler and the flesh of the tubers was minced using a mincer (Model AL 2-1, Bauknecht, W. Germany). The peel and the flesh of the whole the sample were weighed and mixed vigorously to ensure homogeneity separately and sub-samples of 50 g from the peel and the flesh were taken. The sub-samples were kept in a deep freeze in sealed polyethylene bags until analysis.

5.2.6.2 Extraction

An EPA general procedure for extraction trifluralin from various plants was modified to suit trifluralin residue analysis in potato tuber.

The prepared sample (peel or flesh) was placed into a half litre stainless steel blender jar and blended with methanol (AR, May and Baker Ltd, England) in a ratio of 1:3 (75 cm³ for 25 g sample and 150 cm³ for the 50 g sample) for 1 min. The extract was filtered through Whatman No.1 filter paper under vacuum using a Buchner assembly. The blender jar was rinsed with two 25 cm³ portions of methanol and the residue washed in the Buchner funnel with these rinses. The combined extract was transferred to a 1 litre separatory funnel and mixed well with 200 cm³ of 5% sodium chloride (AR, Formachem Ltd, Scotland) solution. The suction flask was rinsed with 50 cm³ of dichloromethane (AR, May and Baker Ltd, England) then the rinse was added to the separatory funnel and shaken for 1 min. The dichloromethane layer was drained through anhydrous sodium sulphate (AR, BDH Ltd, England) into a 250 cm³ round bottom flask. The partition with dichloromethane was repeated twice with other 50 cm³ portions then the anhydrous sodium sulphate was washed with 25 cm³ dichloromethane. The combined dichloromethane was evaporated till dryness using a rotary evaporator (Buchi, Switzerland) at 35°C. The dry flask contents were transferred to a florisil column by five separate portions of 5 cm³ n-hexane (Glass distilled, Rathburn Chemicals Ltd, Scotland) for clean up.

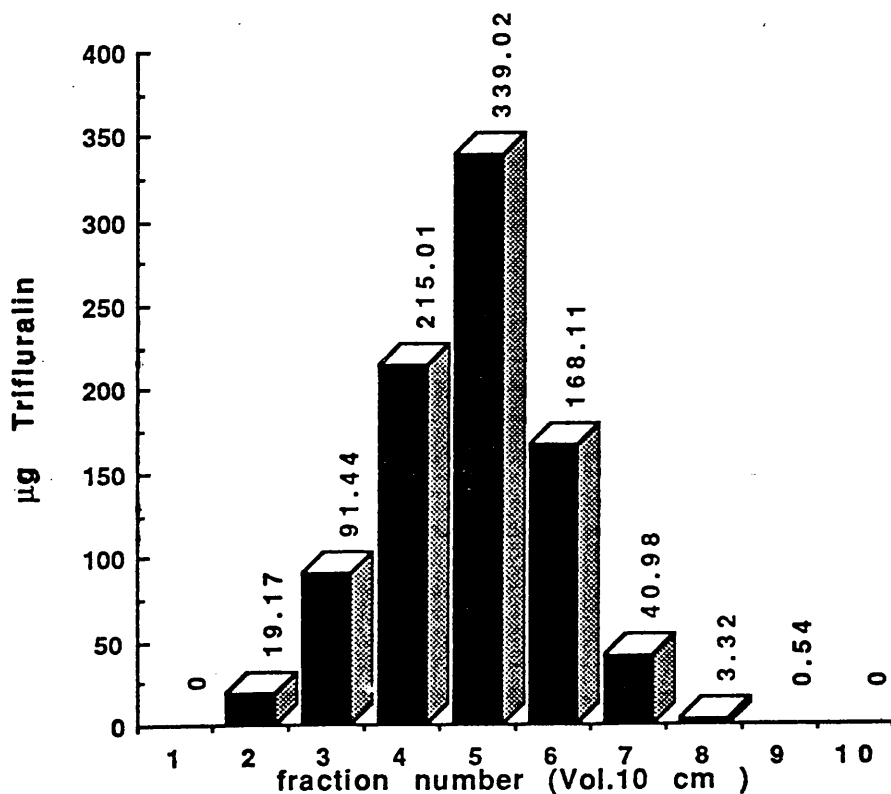
5.2.6.3 Clean-up

The clean-up procedure involved a Florisil column to eliminate the potato tuber co-extracts. This procedure was a modification of the procedure of Tepe and Scroggs (1967). The Florisil column was prepared as follows: A glass wool plug was inserted into a glass chromatography column (25 cm * 1 cm). 2.5 cm of anhydrous sodium sulphate was added then Florisil (60-100 mesh, reagent grade, Aldrich Chemical Co. Ltd, England) was added (after adjusting its moisture content at 6.5%) and the column vibrated until a 10 cm column was formed, then 2.5 cm of anhydrous sodium sulphate was added to the top of the Florisil. The column was prewashed with 25 cm³ of n-hexane, and the hexane was allowed to drain just to the top of the sodium sulphate.

The dry residues were transferred to the top of the Florisil column with five portions of 5 cm³ of n-hexane as mentioned in Section 5.2.6.2, allowing each portion to go into the column before the next portion was added. The first 10 cm³ of hexane were discarded after introducing the extract, then the collection was started and the column was eluted with 100 cm³ of hexane. The eluate was ^{re}ceived in a 250 cm³ round bottom flask. The hexane was evaporated just to dryness using a rotary evaporator at 35°C. The residues of trifluralin were collected with 10 and 2 cm³ volumetric flasks coated with aluminium foil to avoid the light. A gas chromatograph equipped with a FID or ECD detector was used for quantifying trifluralin residues in the peel and the flesh samples respectively.

A profile of trifluralin on the prepared Florisil column was carried out, using a sample of 50 g potato spiked with 1 mg of trifluralin and extracted as mentioned in Section 5.2.6.2 The flow rate of eluted hexane in the Florisil column was adjusted at $1\text{ cm}^3\text{ min}^{-1}$ and each fraction of 10 cm^3 was analysed quantitatively. The profile is presented in Figure 5.1.

Fig.5.1 Elution profile obtained with 1mg of trifluralin on the Florisil column (60-100 mesh, $25\times 1\text{ cm}$, $1\text{ cm}^3\text{ min}$ flow rate, each fraction of 10 cm^3).



5.2.6.4 Determination of trifluralin residues by GC

The optimum conditions for trifluralin determination by gas chromatography (GC) were fixed after trial injections of trifluralin standards in n-hexane.

A Pye 104 (Pye Unicom Ltd, England) gas chromatography, equipped with flame ionization detector (FID) and a silanised glass column (1.66 m * 5mm i.d.) packed with a mixture of 1.5% OV-17 and 1.95% OV-202 on Chromosorb W-HP 100/120 mesh (Alltech Associates/Applied Science) was used for determination of trifluralin residues in the peel samples. The oven and detector temperature were 165 and 250°C respectively. The flow rates of the carrier gas, nitrogen and the detector gases, air and hydrogen (BOC, Glasgow Ltd) were 30, 120, and 30 cm³ min⁻¹ respectively. The sample concentrations were calculated by a comparison with standard solutions using an integrator (Spectra-Physics, SP4290, Burke Electronics, USA).

Hewlett Packard 5890 GC equipped with electron capture detector (ECD) was used for detection of trifluralin residues in the peeled potato tubers treated with 10, 20, 30 mg kg⁻¹ to provide a more sensitive analytical procedure.

The GC was equipped with megabor DB1 15 m with film thickness 1.5 micron (J & W Scientific, INC, USA). The flow rate of nitrogen was 3 cm³ min⁻¹ and the temperatures of injector, column, and detector were 250, 180, and 250°C respectively.

A computing integration system was used for calculation.

5.2.6.5 Recovery study

The recovery study was done using three levels of trifluralin 0.1, 1.0, and 10 $\mu\text{g g}^{-1}$. The spiked samples were processed as described in Sections 5.2.6.2-4. The study was carried out in three replicates for each level. The recovery values were used as correction factor using the nearest value.

5.2.7 Wound healing

This study was carried out in two replicates using potato cultivar Pentland Squire. Trifluralin was applied at three levels (10, 20, and 30 mg kg^{-1}) while the reference compound chlorpropham was applied at the recommended rate of 20 mg kg^{-1} . The application was carried out as mentioned in Section 5.2.3. Prior the application of the chemicals all the potato tubers were wounded using a sharp knife. The control treatment was applied with 25 g alumina only. All treatment were stored in a cold room at $10^{\circ}\text{C} \pm 1$. The boxes containing the treated potatoes were weight at three day intervals throughout the period of this study.

5.2.8 Potato box headspace

This study was carried out using the potato cultivar Maris Piper in two replicates. Trifluralin was applied to the potato tubers in boxes as mentioned in Section 5.2.3. Comparison treatments using empty boxes were carried out at the same treated levels to find the effect of the presence of potato tubers on the trifluralin headspace in the boxes. The levels of application were 10, 20, and 30 mg kg⁻¹. All treatments were kept in a cold room (10°C ± 1).

In this study a Tenax-trap was used to trap trifluralin vapour taken from the box headspace which contained the treated tuber or from the empty box.

Samples were taken using a vacuum desiccator^c which was connected to the top of the Tenax-trap. The latter (Tenax-trap) was connected to the top centre of the box by nuts and teflon washers. 24 h before sampling time all boxes were properly sealed. At the time of sampling a glass tube (5 mm i.d.) was inserted to reach near the box bottom from one top corner of the box to make sure that the sample was withdrawn properly from the box headspace. The samples were taken after 0, 1, 3, and 10 weeks after treatment.

The procedure of using a Tenax-trap for sampling trifluralin vapour and the analytical procedure using the thermal desorption technique were followed as mentioned in Chapter 2.

5.3 RESULTS AND DISCUSSION

5.3.1 Testing the stability of trifluralin on the solid carrier

This test was necessary before deciding to use the neutral aluminium oxide (alumina) as a solid carrier material in preparing the trifluralin dust formulation. The test was carried out in the presence of moisture and at a temperature of 35°C to check the stability of trifluralin on the alumina at these favourable conditions for a possible breakdown. About 96% of the incubated trifluralin on the alumina was recovered after 6 days of incubation. The results indicated that trifluralin was stable under the test conditions hence confirming the stability of trifluralin expected under the potato storage conditions used in this investigation ($10^{\circ}\text{C} \pm 1$).

5.3.2 Preliminary assessment

The preliminary assessment was carried out at the 50 mg kg⁻¹ application level. In this assessment three aspects were investigated, 1- sprout length of treated potato tubers compared with untreated to assess the possible effect of trifluralin as potato sprout suppressant, 2- distribution of trifluralin residues within the potato tuber, and 3- to test the growth of treated tubers.

5.3.2.1 Trifluralin sprout inhibition

The sprout lengths were measured on a 20 tuber sample of three replicates monthly (2nd, 3rd, 4th, and 5th month) and after ten months of storage. The results of sprout length measurement are given in Table 5.1. Plate 5.2 expresses the sprout inhibition effect of trifluralin compared with the chlorpropham and control treatments. The control tubers had sprouted to about 30 mm in length after two months of storage while the treated tubers with trifluralin and that treated with the reference compound chlorpropham showed no sprouting. The sprouting in the control tubers was increasing in length during the 3-5 month period of storage while no sprouting occurred in the treated tubers. At the end of the storage period which was ten months, the sprout lengths reached about 470 mm in the control tubers while no sprouting occurred in trifluralin treated tubers and about 8 mm in chlorpropham treated tubers.

Table 5.1 Mean length of the longest sprout
in the treated potato tubers of
cv. Pentland Squire.

Months after treatment	Mean ^a of sprout length (mm)±SD	Control	Trifluralin ^b	Chlorpropham ^c
2	30.1±04.1	- ^d	-	-
3	61.1±34.4	-	-	-
4	130.5±44.8	-	-	-
5	222.1±64.0	-	-	-
10	470.9±53.3	-	-	8.6±2.6

a mean of 60 sprouts, 20 from each replicate.

b 50 mg kg⁻¹

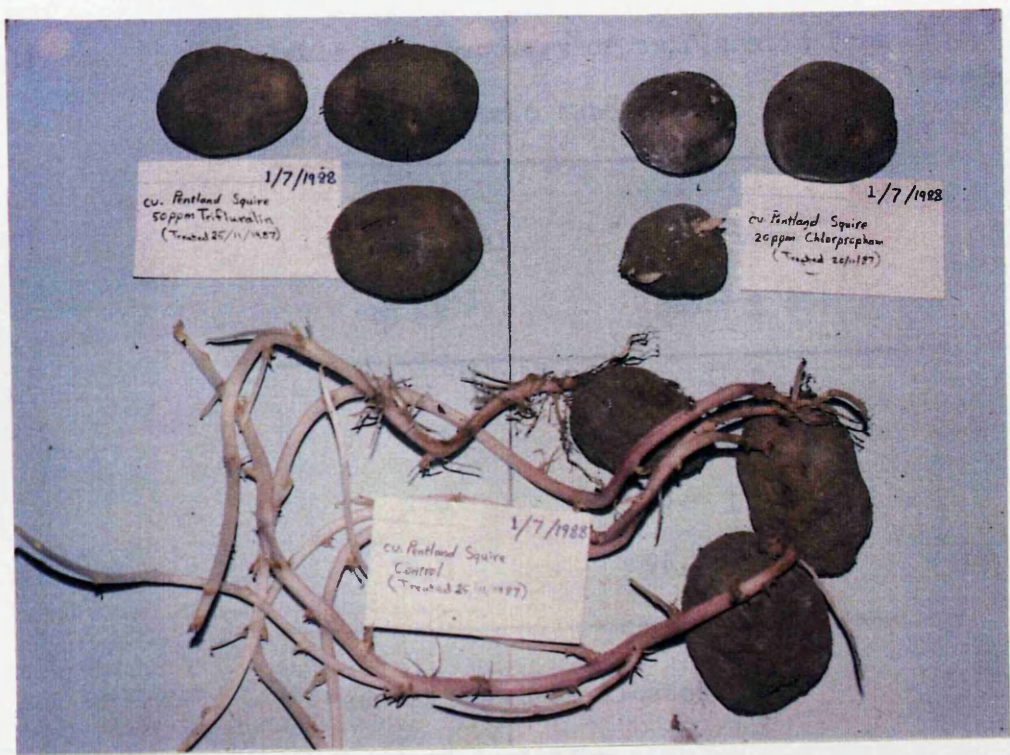
c 20 mg kg⁻¹

d no sprouting

The above results indicate that trifluralin at the 50 mg kg⁻¹ level of application and 10°C was excellent as a potato sprout suppressant for long term potato storage (10 months). These results were encouraging and led on to the idea of assessing different application levels to find the lowest effective level. Various application levels of trifluralin, 30, 20, and 10 mg kg⁻¹ were suggested as being suitable for the assessment.

The effect of trifluralin on the sprouting of tubers was studied in a pot experiment. The tubers were stored at 10 °C for 7 months. The results are shown in Table 5.2. The results showed that trifluralin treatment significantly reduced the sprouting of tubers. The reduction was more pronounced in tubers treated with 20 ppm than in tubers treated with 5 ppm. The results also showed that trifluralin treatment did not affect the weight of tubers. The results of the experiment are summarized in Table 5.2.

Plate 5.2 Treated tubers (cv. Pentland Squire) after 7 months storage at 10 °C.



5.3.2.2 Trifluralin residue distribution within the tuber

Recovery of trifluralin from samples to which trifluralin was added prior to the extraction procedure indicated the efficiency of the modified general analytical method for trifluralin in plant materials for analysing trifluralin residues in potato tubers. The modified method had an average recovery of 93.7%. The results of the recovery study are presented in Table 5.2.

Table 5.2 Recovery of trifluralin from
potato tuber.

Spiked level (mg kg ⁻¹)	% Recovery (Mean ^a \pm SD)
0.1	90.9 \pm 1.7
1.0	93.4 \pm 1.6
10.0	96.7 \pm 1.0

a Mean of three replicates.

SD Standard deviation.

The results of the distribution of trifluralin residues within the potato tuber are shown in Table 5.3. The results showed that virtually all of the residue is in the peel while it was undetectable in the first cm depth and the rest of the flesh. This trend in the distribution of the residues had remained the same throughout the

whole of the storage period. The lowest detection limit of the analytical procedure used in this study was equivalent to 0.04 mg kg^{-1} using GC-FID. An improvement to the sensitivity of the analytical procedure was carried out by using an ECD instead of FID. This improved sensitivity was needed in the assessment of different application levels as the residues were expected to be lower.

The trifluralin residues in the peel were built up throughout the first three months of the storage period and remained nearly constant throughout the remaining seven months. This ^esuggested that the trifluralin in the headspace of ^etreated tubers during the last seven months was present in a adequate amount, if that was not the case, a decline in the residues level in the peel would be expected due to equilibrium between the trifluralin in the headspace of the treated tubers and the residues in the peel of the treated tubers.

Table 5.3 Distribution of trifluralin residues
within potato tuber cv. Pentland Squire.

Months after treatment	Trifluralin residues (mg kg ⁻¹ \pm SD)		
	Peel	1st cm depth	Rest of flesh
1	13.9 \pm 3.3	UN	UN
2	12.3 \pm 1.2	UN	UN
3	15.6 \pm 4.4	UN	UN
4	19.2 \pm 2.2	UN	UN
5	18.0 \pm 4.2	UN	UN
10	17.4 \pm 2.3	UN	UN

UN Undetectable (The lowest detection limit by
using ECD was 2 ng kg⁻¹ fresh weight).

In a similar study using the sprout suppressant tecnazene, Dalziel and Duncan (1980) found that the outer layer of the tuber contains the majority of the tecnazene residues and that there are small but significant amounts of tecnazene distributed throughout the tuber and he reviewed other studies on other sprout suppressants to compare these findings. No residue was detected of chlorpropham below a depth of about 8 mm. Other result with radiochemical techniques indicated that chlorpropham does penetrate more deeply than e.g. tecnazene. More than 70% of the applied chlorpropham was recovered in the peel extract, 5% was recovered from the 10-mm layer beneath the

peel, and 0.2-0.4% was in the extracts from the interior tissue (Coxon & Filmer, 1985). However, Coxon and Filmer (1985) also reviewed that 29.8% of the applied chlorpropham (100 mg kg^{-1}) was present in the outer 1-5 mm layer of peel from washed tubers. Methyl-1-naphthalenate penetrated to a depth of at least 10 mm. Maleic hydrazide, which is a foliar applied, leaves high residues distributed throughout the tuber. There is no apparent specific mechanism by which such penetration occurs and it would appear that diffusion is the most likely method as for chlorpropham. However, it may be that the penetration of the chemical below the peel depends on its water solubility which is for trifluralin 0.5 ppm at ²⁵°C while for tecnazene and chlorpropham it is 0.9 ppm at 20°C and 89 ppm at 25°C respectively.

Many studies on various plants indicate that trifluralin is lipophilic and accumulates in the plant lipid layer. Hilton and Christiansen (1972) reported that trifluralin is lipid-soluble and they studied the impact of lipids on trifluralin uptake and biological effect. In an attempt to study the lipid role in selective action of trifluralin, Hilton (1972) found that the protective action of externally applied lipids was attributed to preventing sorption of trifluralin by seedlings. Probst et al. (1967) reported that root crops, such as onion and garlic contain the trifluralin residue only in the outer shell and in the case of carrots the majority of the trifluralin residue is found only in the peel.

5.3.2.3 A preliminary growth test with treated tubers

After three months of treatment with trifluralin at 50 mg kg^{-1} level, some tubers were freely aerated for one month at room temperature. The one month aeration period caused a reduction in the residue level of trifluralin accumulated in the peel to about half that in the beginning of aeration due to trifluralin volatilization. However, biotransformation (metabolism) by potato tuber, microbial degradation by microbes present in soil coating the tuber and photolysis may be involved in removing residue during airing period especially by photolysis since trifluralin is sensitive to UV light. The residue level at the beginning was 15.6 ± 4.4 while after aeration it became 8.1 ± 3.2 . After two weeks of aeration, sprouting started.

The growth of treated nonaerated, aerated, and control tubers of 1.5-month growth period are shown in Plates 5.3, 5.4, and 5.5 respectively. The growing plants were cut 1 cm above soil and weighed ^tafter two months of growing. The mean of the weights of the three replicates for each treatment were 286.5, 473.8, and 90.6 g for the control, aerated, and nonaerated treatments respectively. An obvious reason for these results is at planting time the control tubers had long and weak sprouts while the aerated tubers had a short and strong sprouts and the nonaerated tubers had no sprouts. These results indicated that aeration of tubers before planting is necessary and the sprout inhibition by trifluralin is reversible. This preliminary assessment study encouraged a further trial to assess the effect of trifluralin on the performance of seed potatoes. This further assessment trial will be the subject of Chapter 6.

Plate 5.3 The growth of potatoes (cv. Pentland Squire) 1.5 months after planting. Treated with trifluralin at a rate of 50 mg kg^{-1} and not aired prior to planting.

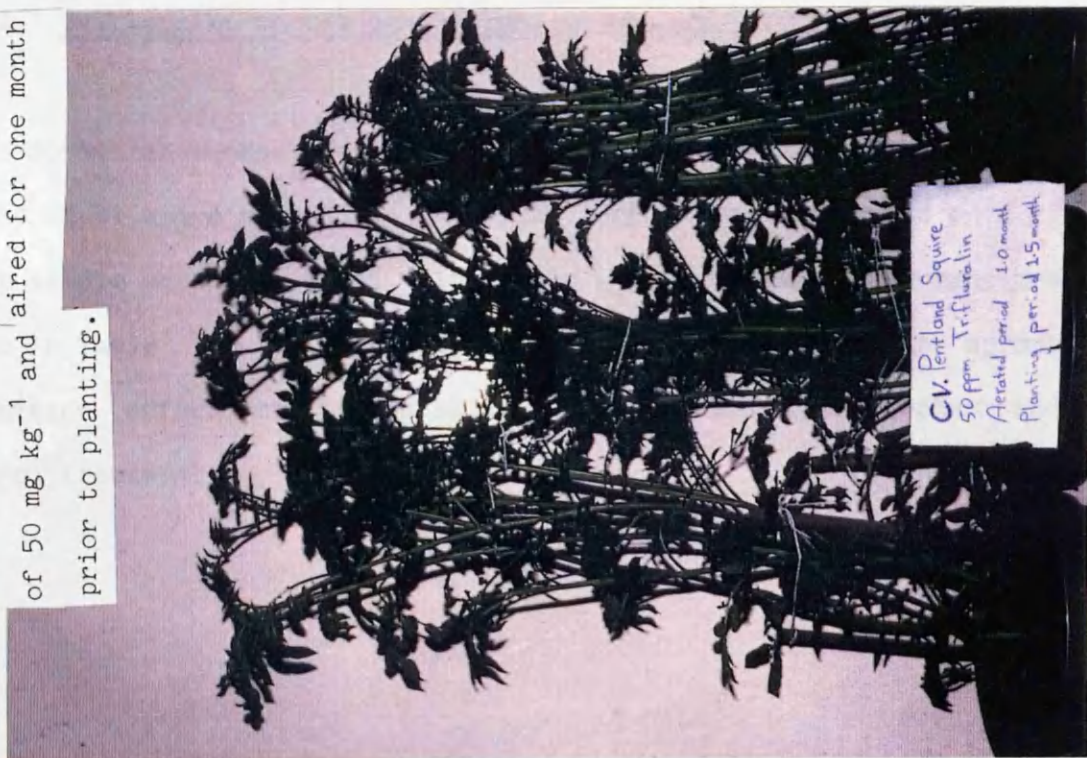


Growth of potatoes (cv. Pentland Squire) 1.5 months after planting. Tubers aired prior to planting for one month.

Plate 5.5 Untreated tubers (Control).



Plate 5.4 Tubers treated with trifluralin at a rate of 50 mg kg⁻¹ and aired for one month prior to planting.



5.3.3 ASSESSMENT OF DIFFERENT LEVELS

This assessment was carried out in large scale compared with the preliminary assessment. Two potato cultivars were used in this assessment, Pentland Squire and Maris Piper. Both were treated on 19 November 1988. The aims of this assessment were to find the lowest effective level of trifluralin which inhibited the sprouting of the two cultivars and also to look at the distribution of trifluralin residues within treated tubers. In addition, the effect of trifluralin on potato wound healing was assessed and an attempt was also made to monitor the trifluralin headspace of the treated boxes.

5.3.3.1 Trifluralin sprout inhibition

Sprout measurements were taken three times throughout the storage period of 31 weeks at $10^{\circ}\text{C} \pm 1$. Sprout lengths were measured on a 25 tuber sample per replicate. The results of sprout measurement are given in Table 5.4. In addition, Plate 5.6 expresses the sprout inhibition effect of trifluralin compared with chlorpropham and control treatments.

Table 5.4 Mean of the longest sprout length of the tubers treated with different levels of trifluralin.

Cultivar	Treatment, treated level, mg kg ⁻¹	Sprout length (mm) (Mean ^a \pm SD) after weeks		
		6	20	31
Pentland	Control	9.0 \pm 3.4	297.5 \pm 89.0	457.1 \pm 183.0
Squire	Trifluralin			
	10	0.1 \pm 0.1	0.2 \pm 0.4	0.2 \pm 0.4
	20	0.0	0.0	0.0
	30	0.0	0.0	0.0
	Chlorpropham ^b			
	20	0.1 \pm 0.2	0.3 \pm 0.3	0.3 \pm 0.2
Maris	Control	34.0 \pm 4.6	184.2 \pm 55.6	285.2 \pm 114.9
Piper	Trifluralin			
	10	1.2 \pm 0.5	1.7 \pm 0.4	2.9 \pm 2.1
	20	1.0 \pm 0.3	0.9 \pm 1.0	1.4 \pm 1.8
	30	0.5 \pm 0.3	1.0 \pm 0.4	1.1 \pm 0.6
	Chlorpropham			
	20	1.3 \pm 0.8	3.0 \pm 1.9	4.0 \pm 1.1
LSD _{0.05} ^c		3.13	59.54	116.38

a Mean of 25 tuber sample/replicate, three replicates.

b Reference compound.

c Least significant difference.

Plate 5.6 Sprout lengths of tubers after 31 weeks storage at 10°C
(Treatments were 10, 20 and 30 mg kg⁻¹ trifluralin, 20 mg kg⁻¹ chlorpropham and control).

(A) cv. Pentland Squire.



(B) cv. Maris Piper.



The results showed that the tubers from the cultivar Maris Piper sprouted earlier and gave shorter sprouts than the cultivar Pentland Squire but not significantly so according to analysis of variance . The mean sprout length of Maris Piper was 34.9 mm and that of Pentland Squire was 51.0 mm. The analysis of variance showed that the control treatment was different from other treatments while no significant difference between trifluralin treatments (three levels) and the treatment of the reference compound chlorpropham was noted. The sprout suppression by trifluralin at the lowest level (10 mg kg^{-1}) seemed to be more effective than chlorpropham under these assessment conditions. The sprout length was obviously increasing with time but due to the variability involved this increase was not statistically significant.

5.3.3.2 Distribution of trifluralin residues within the treated tuber

The peel of the washed potato tuber and the peeled tuber itself were analysed for trifluralin residues. GC-FID was used to quantify the trifluralin residues in the peel as most the residues accumulated in the peel while GC-ECD was used for the peeled tuber to provide high sensitivity as the residues of trifluralin were undetectable in the potato flesh in the preliminary assessment. The lowest detection limit using GC-ECD was equivalent to 2 ng kg^{-1} fresh weight of tubers. The level of the detected residue in the peeled tuber was equal to background for the control treatment. This finding means there is no significant amount of trifluralin in the peeled tuber (flesh). The results for the trifluralin residues are shown in Table 5.5.

Table 5.5 Trifluralin residues in treated potato tubers at different levels.

	Treatment level,	Mean ^a residues in peel (mg kg ⁻¹) after weeks				
Cultivar	(mg kg ⁻¹)	3	10	18	23	31
Pentland						
Squire	10	4.0±0.3	5.5±1.2	5.6±1.2	5.7±0.7	5.9±1.0
	20	8.9±1.3	11.3±0.8	10.5±1.2	9.1±1.7	8.6±1.0
	30	10.4±1.0	10.8±1.6	12.5±2.7	14.3±1.4	11.1±1.5
LSD _{0.05} ^b		1.97	2.43	3.64	2.69	2.40
Maris						
Piper	10	6.4±1.5	8.5±2.4	9.8±3.0	10.4±0.6	7.9±1.5
	20	10.1±1.4	11.0±1.0	12.6±1.1	13.2±3.6	13.2±3.8
	30	15.5±2.5	15.2±3.3	17.2±1.1	20.1±1.7	21.0±1.5
LSD _{0.05}		3.72	4.88	3.84	4.63	5.66

a Mean of three replicate \pm SD

b Least significant difference

^a
Virtually all of the residues were located in the peel of the treated tubers and undetectable in the rest of the tuber (flesh) according to the lowest detection limit ²
(ng kg⁻¹) of the analytical method using ECD.

The analysis of variance showed that the difference between the two investigated cultivars were highly significant in term of residues. The mean residue value for Pentland Squire was 8.9 and that for Maris Piper was 12.8 mg kg⁻¹. This difference may be due to differences in peel thickness or in composition between the two cultivars.

The levels of trifluralin adopted caused highly significant differences in the levels of the residues in the peel of the treated tubers. The mean residues were 6.9, 10.9, and 14.8 mg kg⁻¹ which corresponded to the treatment levels of 10, 20, and 30 mg kg⁻¹ respectively. Since the trifluralin is lipid-soluble more trapping trifluralin would be expected to be trapped in the peel with increasing treatment level.

The residue level did not differ significantly with time, due to the equilibrium between the trifluralin in the tuber peel and the trifluralin in the headspace.

5.3.3.3 Wound healing

Due to a problem with relative humidity no differences between all the weight measurments were noted. All the cut surfaces in the treated tubers dried out and no rotting symptoms were observed.

5.3.3.4 Headspace of trifluralin in the potato box

A sensitive analytical technique was used in the study to monitor the headspace of treated tubers for trifluralin throughout the storage period. This was attempted along the lines of the procedure adopted for other volatile chemicals. Unfortunately, the sampling procedure was not very accurate resulting in an unacceptable degree of variability.

CHAPTER 6

THE EFFECT OF TRIFLURALIN ON THE PERFORMANCE OF SEED POTATO TUBERS

This Chapter deals with the effects of different application levels of trifluralin on the subsequent performance of treated seed tubers. This study was based on the promising results of the preliminary growth test on trifluralin treated potatoes with 50 mg kg⁻¹ a.i. which was carried out as a part of the preliminary assessment (Chapter 5).

6.1 Introduction

Excessive sprout growth during storage is a major problem for seed potato producers. Long and spindly sprouts are easily broken or damaged during the subsequent handling and planting operations, particularly during automatic planting. The requirement is for a short sturdy sprout strongly attached to the tuber. The optimum length of sprout varies according to a number of considerations including variety of potato, however lengths from 5-20 mm are advised (Nash, 1978).

In Scotland traditionally much of the seed potatoes were treated with tecnazene. Seed growers can use tecnazene as a fungicide for control of dry rot and its sprout suppressant property is an added advantage but not the sole reason for its use (Dalziel, 1978). Dalziel (1978) also reviewed that chlorpropham and propham are

unsuitable for the treatment of seed. Maleic hydrazine cannot be used as a sprout suppressant on crops intended for seed because it destroys apical dominance leading to the development of a large number of active eyes and the true sprouts do not develop. The Seed Potato Regulations (1984) in U.K. prohibit the use of sprout suppressant chemicals on potatoes certified as seed.

It is well known that seed tubers contaminated with the sprout suppressant, chlorpropham fail to emerge. Boyd (1988) studied the effect of chlorpropham on the performance of seed tubers. She concluded that seed tubers containing chlorpropham residues of $<0.2 \text{ mg kg}^{-1}$ grow successfully with little effect on the mean emergence time while with residues of 0.2 mg kg^{-1} a decrease in total yield by approximately 15% is observed. Residues of $0.3 - 1 \text{ mg kg}^{-1}$ cause a delay in mean emergence time of 14 days, decrease total emergence and subsequently decrease medium and large yield and also total yield. Chlorpropham residues of $>1 \text{ mg kg}^{-1}$ cause drastic effects on total emergence (50%) and total yield. In addition to seed potato growth problems resulting from exposure to chlorpropham, cereal seed germination and growth can also be badly affected by residues from previous applications.

It is only tecnazene which has widespread commercial acceptability as a fungicide and sprout suppressant for seed, especially in a major seed producing country such as Scotland (Dalziel, 1978). In an assessment by Dalziel and Duncan (1975) it was found that the treatment of tubers by tecnazene at a rate of 100 mg kg^{-1} led to a significant increase in mean emergence time and reduction in yield. This assessment was carried out with the cultivar Golden Wonder stored in 50 kg bins and aerated for one month prior to planting.

A searching for a suitable sprout suppressant for the storage of seed potatoes is very necessary since the recommended compound (tecnazene) has been associated with problems.

Due to the reversal of the inhibition action of trifluralin and its ability to be removed by volatilization from treated tubers which was noted in the preliminary growth test of treated tubers (Chapter 5), an assessment was carried out to assess the effect of various levels of trifluralin application on the performance of seed potatoes. Chlorpropham was used as a reference^e compound in this assessment as it affected sprouting by interfering with the cell division process.

6.2 Experimental

6.2.1 Materials

All materials used such as trifluralin, chlorpropham, organic solvents(n-hexane, methanol and dichloromethane), neutral aluminium oxide, anhydrous sodium sulphate and sodium chloride were as previously described in the experimental section of Chapter 5.

Seed of cultivars Pentland Squire and Maris Piper were purchased from a local farm.

6.2.2 Treatment of seed potato tubers

Two cultivars were used in this work and each treatment was carried out in duplicate for each level of application and for each cultivar. The potato sprout suppressant, chlorpropham was used as a reference compound.

Trifluralin and chlorpropham were applied to the potato tubers in 10 kg boxes as mentioned in Section 5.2.3, Chapter 5. Trifluralin was applied at three levels 10, 20, and 30 mg kg⁻¹ while chlorpropham was applied at the commercial rate of 20 mg kg⁻¹. All treatments were kept in a cold room 10°C[±]1 in cardboard boxes with loosely fitting lids for ~17 weeks, from 19 November 1988 until 20 March 1989.

6.2.3 Airing

After the storage period of 17 week, all the treated tubers were free by aired by spreading them as one layer of tubers for a period of 6 week in a greenhouse. The tubers in this period were exposed to the day light and to a temperature average between 15-22°C. The airing started on 21 March 1989 until the planting time 2 May 1989. Before airing and before planting 1kg samples were taken for residues analysis.

6.2.4 Planting

The field experiment was carried out at Arkleston farm, Paisly, Renfrewshire, Glasgow and consisted of a sandy loam soil. The soil was uniformly treated with potato fertilizer.

The tubers were planted by hand on 2 May 1989 at 250 mm spacing.

6.2.5 Experimental design

The experiment was planted in two independently randomised blocks. A cultivar, Desiree was planted out as guard drills between treatments and arround the blocks. Each block consisted of 5 plots and each plot consisted of 6 drills. The tubers were planted 13 per drill.

6.2.6 Emergence

Numbers of emerged sprouts were taken at 2 day intervals from 24 May until 3 June except the last two were taken at 4 day intervals from 3 to 11 June for each drill.

6.2.7 Harvesting and grading

The crop was mechanically exposed then each drill was hand lifted into 12 kg net sacks and weighed. The yield of each drill was graded over 52 mm and 32 mm riddles and the yield of each drill was recorded as >45 or <45 mm.

6.2.8 Residue analysis

Washed 1 kg samples were analysed before and after the airing period for residues of trifluralin in the peel of the tuber. The analysis was carried out as mentioned in Section 5.2.6, Chapter 5.

6.3 Results and discussion

6.3.1 Residues

Trifluralin residues in tuber peel before and after airing are presented in Table 6.1. The results showed that the residues in tuber peel increased with increasing applied amount. The same trend was noted in both investigated cultivars. This difference was discussed in Section 5.3 of Chapter 5 when the distribution of trifluralin residues was investigated in both cultivars.

Table 6.1 Trifluralin residues in tuber peel before and after the airing period.

Cultivar	Treat. level ^a	Residues ^b		%Remaining residue after airing
		Before	after	
Pentland	10	6.09	1.86	30.54
Squire	20	11.17	3.59	32.14
	30	13.81	4.10	29.69
Maris	10	7.77	5.43	69.88
Piper	20	12.17	9.45	77.65
	30	16.54	14.07	85.07

a mg kg⁻¹

b Mean of two replicates, mg kg⁻¹ after 6 week period of airing. Overall LSD_{0.05} are 1.95 and 2.33 for the cv. Pentland Squire and Maris Piper respectively.

It is clear that airing for 6 weeks prior planting reduced the residue levels by a very significant amount, especially with the cultivar Pentland Squire. The residues were lost from Pentland Squire tuber peel much more than that from Maris Piper. About 70% of the trifluralin residues were lost from Pentland Squire while a range of 15-30% depending on the treatment level was lost in case of Maris Piper. This finding could be due to the differences in the thickness and the composition of the periderm. The main factors which causes the loss in residues during the airing period, volatility and photolysis since the trifluralin is a volatile compound and sensitive to UV light while there is a possibility to the biotransformation and microbial degradation by soil microbes taking place over an extended period.

The level of the trifluralin residue at the planting time seems to have no significant effect on the percentage of the emerged plants after 42 days of planting and the total yield. This will be discussed later in a following sections.

6.3.2 Sprouting and Emergence

On the planting time the mean sprouts of the control tubers were 274 and 117 mm for Pentland Squire and Maris Piper respectively in contrast to the treated tubers which showed short and strong sprouts in a range of 5-20 mm. Plate 6.1 gives an impression of the degree of sprouting of the investigated cultivars after a 6 week period of free airing.

Emergence assessment is very necessary to assess how the seed tubers would perform in the field. The results of the effect of the trifluralin residues at planting time on the percentage of emerged plants are shown in Table 6.2.

Table 6.2 Effect of trifluralin on the emergence of treated seed tubers.

Cultivar	Treatment,	Residue at	% Emergence after day	
	treat. level ^a	planting time ^b	22	42
Pentland	Control	-	96.2	100
Squire	Trifluralin			
	10	1.86	96.2	100
	20	3.59	82.0	100
	30	4.10	79.5	98.7
	Chlorpropham			
	20	-	25.7	39.8
Maris	Control	-	100	100
Piper	Trifluralin			
	10	5.43	85.9	100
	20	9.45	76.9	100
	30	14.07	79.5	96.2
	Chlorpropham			
	20	-	24.4	41.0

a mg kg⁻¹

b Mean of two replicates, mg kg⁻¹ after a 6 week period of airing.

Plate 6.1 Sprout lengths of tubers after 17 weeks of treatment and 6 weeks of airing at 15-22°C (Treatments were 10, 20 and 30 mg kg⁻¹ trifluralin, 20 mg kg⁻¹ chlorpropham and control).

(A) cv. Pentland Squire.



(B) cv. Maris Piper.



The results showed that trifluralin did not significantly affect emergence after 42 days of planting in comparison with control treatments in both cultivars. The reference compound, chlorpropham badly affected the emergence of treated tubers. After 42 days of planting the emergence for control and trifluralin level of 10 and 20 mg kg⁻¹ were 100% for both investigated cultivars except for the highest level of trifluralin where it was 98.7 and 96.2% for Pentland Squire and Maris Piper respectively.

Chlorpropham had about the same effect in reducing the emergence percentage of treated seed tubers for both investigated cultivars. After 42 days of planting the mean emergence were 39.8 and 41.0% for Pentland Squire and Maris Piper respectively. Plate 6.2 gives a representative image after 23 days of planting time. The reduction effect of chlorpropham was very clear and could be seen as a blank area while the other treatments (control and trifluralin levels) had about the same planting density.

Plate 6.2 Growth image of tubers after 23 days of planting time (Treatments were 10, 20 and 30 mg kg⁻¹ trifluralin, 20 mg kg⁻¹ chlorpropham and control, aired for 6 weeks at 15-22°C prior to planting). General view of the experimental area.



Table 6.3 Effect of trifluralin on the yield of treated seed potatoes.

<u>Cultivar</u>	<u>Treatment,</u> <u>treat. level^a</u>	<u>Residue at</u> <u>planting time^b</u>	<u>Yield</u>		
			<u>Total</u> <u>(kg)^c</u>	<u><45 mm</u> <u>(%)^d</u>	<u>>45 mm</u> <u>(%)^e</u>
Pentland	Control	-	19.4±1.3	6.4±3.0	93.6±3.0
Squire	Trifluralin				
	10	1.86	21.6±2.3	7.8±2.2	92.2±2.2
	20	3.59	20.3±1.6	8.3±2.6	91.7±2.6
	30	4.10	20.0±2.4	7.0±1.5	93.0±1.5
	Chlorpropham				
	20	-	10.4±2.2	7.4±1.0	92.6±1.1
Maris	Control	-	22.2±2.1	24.4±5.6	75.6±5.6
Piper	Trifluralin				
	10	5.43	21.5±3.1	20.1±4.4	79.9±4.4
	20	9.45	20.9±2.2	20.6±5.6	79.4±5.6
	30	14.07	22.6±2.4	15.3±3.2	84.7±3.2
	Chlorpropham				
	20	-	11.3±4.1	17.1±6.7	82.9±6.7
LSD _{0.05}			2.86	0.97	2.59

a mg kg⁻¹b Mean of two replicates, mg kg⁻¹ after 6 week period of airing.

c Mean of 6 drills±SD

d %Seed potatoes, Mean of 6 drills±SD

e %Ware potatoes, Mean of 6 drills±SD

6.3.3 Yield

The results of the effect of various trifluralin application levels on the ratio of seed/ware potatoes and the total yield are given in Table 6.3.

Analysis of variance showed a highly significant treatment effect on the total yield. The significance was due to chlorpropham treatment but was not noted between trifluralin treatments. The means of total yield were 10.8, 20.8, 21.5, 20.6, and 21.3 kg for chlorpropham, control, 10, 20, 30 mg kg⁻¹ of trifluralin treatments respectively.

The treatment effect was also significant in producing <45 mm tubers and was highly significant in producing >45 mm tubers. These significant effects were also due to the chlorpropham treatment.

The cultivar effect on producing seed tubers was highly significant. The mean in a seed percentage basis of the total yield was 7.4% for the cultivar Pentland Squire while it was 19.5% for Maris Piper.

The block and replicate effects were not significant factors effecting the total yield or the size distribution of tubers (<45 and >45 mm).

CHAPTER 7

GENERAL CONCLUSION

As stated in Chapter 1, the first aim of this thesis was to investigate the environmental fate of the dinitroaniline herbicide trifluralin concerning the main two pathways of trifluralin dissipation in the environment. These pathways are volatilization and photodecomposition. The second aim was to assess the possible alternative use of trifluralin as a potato sprout suppressant.

In Chapter 1, it was very clear from the reviewed literature that the most important pathways for the dissipation of trifluralin in the environment were 1- its volatility from treated surfaces especially from soil in which trifluralin is usually incorporated and 2- that trifluralin is sensitive to UV light. Both these dissipation pathways of trifluralin are very important from environmental point view and the efficiency of trifluralin in controlling weeds especially under Iraqi climate conditions, long hot summer and sunny most of the year. However, trifluralin at recommended rate of use does not give satisfactory results in weed control and this leads to use some time double the recommended rate especially during the summer.

In Chapter 2, the volatilization of trifluralin from soil was studied. In this study three types of soils differing in organic matter content were used. The study was carried out under different conditions such as different soil moisture contents and different temperatures.

A laboratory model of an air flow soil system was found suitable to carry out the volatility study under a dynamic system to mimic what is happening in the environment, viz an air flow removing the vapours from above the treated soil. This system was found to work successfully during the course of this study. Since a large number of agrochemicals are applied to soil under different conditions such as temperature, wind flow speed, soil type and soil moisture content, these factors which effected the volatility could be studied using such a laboratory model to get a preliminary forecast about the degree of dissipation of the soil applied chemical.

It was necessary to adopt a sensitive analytical method to detect quantitatively trifluralin vapours in the headspace of treated soil. Because of the low level of trifluralin headspace under certain circumstances it was found necessary to use a sampling technique to provide a preconcentration of the trifluralin vapour in order to reach the detection level of the GC instrument. This kind of sampling was accomplished successfully using a Tenax-trap. The required sensitivity was achieved using a Tenax-trap coupled with thermal desorption.

From the headspace analytical method it was concluded that the gas chromatography/desorption technique was satisfactory. Trifluralin was quantitatively introduced into the gas chromatography column using the desorption method which has no dilution factor. The sample on the Tenax-trap could be stored for up to five days with no significant sample loss at 5°C. This property permits the transport of the samples from the sampling area, which may be well away from the laboratory prior to analysis.

From the results of the volatility study, it was concluded that the soil type is an important factor effecting the volatility and that this was mainly due to the organic matter content (O.M.). The loss from acid washed ~~sand~~ (0.0% O.M.) was very great compared with that of the other two soils. In the comparision between the Iraqi soil (2.8% O.M.) and the Scottish Arkleston soil (7.5% O.M.), the loss was more from the Iraqi soil but this was not significant. This organic matter effect was confirmed by an adsorption study in which it was found that trifluralin adsorbed on Scottish Arkleston soil > Iraqi soil > acid washed sand.

The effect of moisture content in this study was found to be more pronounced than either soil type or temperature. The volatility increased greatly with increasing moisture content. This trend of increasing loss was found to be affected by soil texture. Under field capacity the Iraqi soil (clay loam) lost trifluralin vapour at lower rate than under half field capacity. This effect may be due to the reduction in the porosity of the soil.

An increase in temperature enhanced the volatility of trifluralin from all the investigated soils at all moisture contents studied but compared with soil type and moisture content the effect was less.

The distribution of trifluralin residues between the top and bottom layers of treated soil showed that may be trifluralin vapour condensed on the top layer especially when the diffusion of trifluralin was relatively high at a soil temperature of 40°C and the soil surface temperature was less (near 20°C). Practically this phenomenon

could happen in the field especially where there is a big difference in temperature between day and night.

In Chapter 3, the photodecomposition of trifluralin was studied in different media and the effect of some additives on the photolysis rate in methanol was investigated. In addition, the identification of possible photoproducts in different media was also investigated. In this study a similar UV wavelength to that which possibly reached the earth surface (~ 290 nm) was used.

It was concluded from the results of photolysis in n-hexane, methanol, acetonitrile, and distilled water that trifluralin photolysis was dependent on the donation of hydrogen from the medium. It was found that trifluralin photolysed more in n-hexane and much less in the acetonitrile. This result is in agreement with the fact that reduction is an important reaction in the trifluralin breakdown.

The effective additives in the reduction of trifluralin photolysis rate were the pigments such as chlorophyll, methylene blue, and crystal violet. The crude chlorophyll extract was the most effective. Chlorophyll (crude extract) could be used in the formulation in terms of regulating the persistence of trifluralin if this property is required.

Because of the high sensitivity of trifluralin to UV light, the free radical scavenger additives such as KCNS and PABA did not reduce the trifluralin photolysis rate significantly.

The emulsifiable concentrate formulation of trifluralin was found to be much more resistant to the effect of UV light than that of the chemical itself.

It could be concluded that the trifluralin photolysis varied in the environment depending on the media such as organic or aquatic in addition to the effect of the presence of some substances in these different media.

Generally, the identified trifluralin photoproducts in this work can be classified into three groups: (1) dealkylation of N-propyl groups or reduction of nitro groups and a combination of both, (2) benzimidazole derivatives formed by cyclization, and (3) dimers in the form of azo and azoxy derivatives.

Twelve trifluralin photoproducts were identified in the three investigated media. Three of the twelve identified photoproducts were identified as trifluralin photoproducts for the first time. Two other photoproducts more likely dimers remained unidentified. In addition, with many others, it was very hard to get clear mass spectra for them. More investigation should be carried out in this field to identify all possible trifluralin photoproducts to provide a clear picture of this aspect.

The second aim of this thesis as mentioned before was to assess the possible alternative use of the herbicide trifluralin as a potato sprout suppressant. Trifluralin has never been assessed previously in terms of potato sprout suppressant activity but due to the similarity of trifluralin to some of the commercial potato sprout suppressants

already under study in the laboratory, the idea behind carrying out this assessment was born (Chapter 4).

The preliminary assessment in Chapter 5 revealed trifluralin at 50 mg kg^{-1} to be an effective potato sprout suppressant for tubers stored at 10°C on long term storage (10 months) compared with the commercial potato sprout suppressant chlorpropham at a rate of application of 20 mg kg^{-1} .

Airing of treated potatoes for one month after three months of treatment was sufficient to reduce the trifluralin residues to a level that allowed the treated tubers to sprout. In addition, the aired tubers produced healthy potato plants comparable to that produced from untreated tubers. This means when the influence of trifluralin is removed cell division can be back to normal i.e. the effect of trifluralin on cell division is reversible. This is a very important property concerning the use of trifluralin on seed potatoes. The reversible effect was also reported by Talbert (1965) when he noted the resumption of soybean root growth and cell division after 24 h exposure in the low concentration of trifluralin followed by the subsequent loss of trifluralin from the nutrient solution by volatilization.

As a result of the preliminary assessment in Chapter 5 which indicated that trifluralin at 50 mg kg^{-1} of potatoes was able to suppress sprouting completely, it was decided to search for the lowest effective level of application. In an assessment of the effect of many application levels it was found that a level of application of 10 mg kg^{-1} was very effective at inhibiting potato sprouting throughout a

storage period of 31 weeks at 10°C. This effective level is clearly lower than that of the commercial potato sprout suppressants chlorpropham (20 mg kg⁻¹) and tecnazene (120 mg kg⁻¹).

The residue analysis results showed nearly all the trifluralin residues had accumulated in the tuber peel while residues were undetectable in the peeled tuber. This finding is very important indeed from the potato consumption point of view.

The reversible effect of trifluralin on cell division encouraged an assessment of the effect of trifluralin on the performance of treated seed potatoes in some detail (Chapter 6).

The subsequent field trial results indicated that trifluralin did not effect emergence at any of the application levels used compared with a control treatment while chlorpropham had an adverse effect, reducing the emergence by about 60% 42 days after planting. The same trend was reflected in the total yield. The total yield of trifluralin treated tubers was not significantly different from that of untreated tubers while chlorpropham reduced the total yield to approximately half.

The seed/ware potato ratio was not affected by trifluralin treatment but it did vary with cultivar.

Many more studies must be carried out to get a clearer picture of the ability of trifluralin to act in this field before it could be recommended for commercial use. However, trifluralin could work effectively even at lower levels than was found effective in this

work (10 mg kg^{-1}). Problems with the wound healing assessment meant that this aspect should be repeated under correct humidity conditions as this facet is very important for sound potato storage. The trifluralin headspace analytical method (Chapter 2) provides a good aid to monitor the trifluralin headspace in the potato store and could be introduced as a useful management tool as it could also be used for monitoring other volatile chemicals present in commercial potato stores or widened even further to include other stored produce.

REFERENCES

- ANON. (1988). Potato statistics for Great Britain. Historical data-1960 onwards. Potato Marketing Board publication.
- ANON. (1985a). Historical data summary from 1955. Potato Marketing Board, London.
- ANON. (1985b). Potato statistics bulletin. Potato Marketing Board, London.
- ALEXANDER, M. (1980). Biodegradation of toxic chemicals in water and soil. In: Dynamics, exposure and hazard assessment of toxic chemicals (Ed. R. HAQUE). pp 179-190. Ann Arbor Sci., Ann Arbor.
- ANDERSON, W.P., RICHARDS, A.B. and WHITWORTH, J.W. (1968) Leaching of trifluralin, benefin and nitralin in soil columns. Weed Sci. 16: 165-168.
- APPLEBY, A.P. and VALVERDE, B.E. (1989). Behaviour of dinitroaniline herbicides in plants. Weed Technol. 3: 198-206.
- ASHTON, M. and CRAFTS, A.S. (1973). Mode of action of herbicides. John Wiley and Sons, New York.
- ATLAS, E.L. and SULLIVAN, K.F. and GIAM, C.S. (1985). Preconcentration of atmospheric organic compounds by heat desorption and solvent microextraction. Anal. Chem. 57: 2417-2419.
- AUDUS, L.J. (1960). Microbiological breakdown of herbicides in soils. In: Herbicides and soil (Ed. E.K. WOODFORD and G.R. SAGAR). pp 1-19. Black Well Sci., Oxford.
- BAILEY, G.W. and WHITE, J.L. (1964). Review of adsorption and desorption of organic pesticides by soil colloids, with implications concerning pesticide bioactivity. J. Agric. Food Chem. 12: 324-332.
- BARDSLEY, C.E., SAVAGE, K.E. and WALKER, J.C. (1968). Trifluralin behaviour in soils. II. Volatilization influenced by concentration, time, soil moisture content, and placement. Agron. J. 60: 89-92.
- BARTELS, P.G. and HILTON, J.L. (1973). Comparison of trifluralin, oryzalin, pronamide, propham, and colchine treatment on microtubules. Pestic. Biochem. Physiol. 3: 462-472.
- BAYER, D.E., FOY, C.L., MALLORY, T.E. and CUTTER, E.G. (1967). Morphological and histological effects of trifluralin on root development. Amer. J. Bot. 54: 945-952.
- BEVERIDGE, J.L., DALZIEL, J. and DUNCAN, H.J. (1981). The assessment of some volatile organic compounds as sprout suppressants for ware and seed potatoes. Pot. Res. 24: 61-76.

- BILLINGS, W. and BIDDLEMAN, T.F. (1980). Field comparison of polyurethane foam and Tenax-GC resin for high-volume air sampling of chlorinated hydrocarbons. *Environ. Sci. and Technol.* 14: 679-683.
- BISWAS, P.K. and HAMILTON, W.Jr. (1969). Metabolism of trifluralin in peanuts and sweet potatoes. *Weed Sci.* 17: 206-211.
- BODE, L.E., DAY, C.L., GEBHARDT, M.R. and GOERING, C.E. (1973). Mechanism of trifluralin diffusion in silt loam soil. *Weed Sci.* 21: 480-484.
- BOYD, I.M.G. (1988). Ph.D. thesis. University of Glasgow.
- BOYD, W.D. (1984). Ph.D. thesis. University of Glasgow.
- BOYD, W.D. and DUNCAN, H.J. (1986). Studies on potato sprout suppressants. 6. Headspace analysis of tecnazene and chlorpropham in a commercial box potato store. *Pot. Res.* 29: 207-216.
- BRAITHWAITE, A. and SMITH, F.J. (1985). *Chromatographic methods*. Chapman and Hall, London.
- BREWER, F., LAVY, T.L. and TALBERT, R.E. (1982). Effect of flooding on dinitroaniline persistence in soybean (*Glycine max*)-Rice (*Oryza sativa*) rotations. *Weed Sci.* 30: 531-539.
- BROCKMAN, F.E., DUKE, W.B. and HUNT, J.F. (1975). A rainfall simulator for pesticide leaching studies. *Weed Sci.* 23: 533-535.
- BROWN, W. (1947). Effect of chlorinated nitrobenzenes on the sprouting of potato tubers. *Ann. Appl. Biol.* 34: 422-429.
- BURTON, W.G. (1966). The potato: a survey of its history and of factors influencing its yield, nutritive value, quality and storage. Veenman and Zonen, Wageningen, Holland.
- CALVET, R. (1980). Adsorption-Desorption phenomena. In: *Interactions between herbicides and the soil* (Ed. R.J. HANCE). pp 1-30. Academic Press, London,
- CARTER, G.E., Jr. and CAMPER, N.D. (1975). Soil enrichment studies with trifluralin. *Weed Sci.* 23: 71-74.
- COFFEY, D.L. and WARREN, G.F. (1969). Interaction of herbicides by activated carbon and other adsorbents. *Weed Sci.* 17: 16-19.
- COHEN, S.Z., ZWEIG, G., LAW, M., WRIGHT, D. and BONTOLYAN, W.R. (1978). Analytical determination of N-nitroso compounds in pesticides by the united states Environmental Protection Agency-A preliminary study. In: *Environmental aspects of N-nitroso compounds* (Ed. E.A. WALKER, M. CASTEGNARO, L. GRICITTE and R.E. Lyle). pp 333-343. IARC Scientific Publications, Lyon.
- CORBETT, J.R., WRIGHT, K. and BAILLIE, A.C. (1984). *The biochemical mode of action of pesticides*. Academic Press, London.

- COUTANT, R.W., LEWIS, R.G. and MULIK, J. (1985). Passive sampling devices with reversible adsorption. *Anal. Chem.* 51: 219-223.
- COXON, D.T. and FILMER, A.A.E. (1985). The fate and distribution of chlorpropham when applied to store potatoes as a sprout suppressant. *Pestic. Sci.* 16: 355-363.
- CRIPPS, R.E. and ROBERTS, T.R. (1978). Microbial degradation of herbicides. In: *Pesticide microbiology* (Ed. I.R. HILL and S.J.L. Wright). pp 669-730. Academic Press, London.
- CROSBY, D.G. (1972). Environmental photooxidation of pesticides. In: *Degradation of synthetic organic molecules in the biosphere. Proceeding of a conference, San Francisco, California, June 12-13, 1971.* pp 260-278. National Academy of Sciences, Washington.
- CROSBY, D.G. (1976). Herbicide photodecomposition, In: *Herbicides: chemistry, degradation and mode of action, Vol. 2* (Ed. P.C. KEARNEY and D.D. KAUFMAN). pp 835-889. Marcel Dekker, INC., New York.
- CROSBY, D.G. (1979). The significance of light induced pesticide transformations. In: *Advances in pesticide science, Part 3, Vol. 3* (Ed. H. GEISSBHLER). pp 568-576. Pergamon Press, Oxford.
- CROSBY, D.G. and LEITIS, E. (1973). The photodecomposition of trifluralin in water. *Bull. Environ. Contam. Toxicol.* 10: 237-241.
- CROSBY, D.G. and LI, M. (1969). Herbicide photodecomposition. In: *Degradation of herbicides* (Ed. P.C. KEARNEY and D.D. KAUFMAN). pp 321-362. Marcel Dekker, INC., New York.
- CROSBY, D.G. and MOILANEN, K.W. (1972). 163rd National meeting of the American Chemical Society, Boston, Mass., April 1972. Abstract PEST-27.
- DALZIEL, J. (1978). Ph.D. thesis. University of Glasgow.
- DALZIEL, J. and DUNCAN, H.J. (1975). Studies on potato sprout suppressants. 2. Effect of tecnazene on subsequent growth of seed potatoes. *Pot. Res.* 18: 92-97.
- DALZIEL, J. and DUNCAN, H.J. (1980). Studies on potato sprout suppressants. 4. The distribution of tecnazene in potato tubers and the effect of processing on residue levels. *Pot. Res.* 23: 405-411.
- DILLING, W.L. (1982). Atmospheric environment. In: *Environmental risk analysis for chemicals* (Ed. R.A. CONWAY). pp 154-197. Van Nostrand Reinhold Company, New York.
- DOWNER, G.B., HALL, M. and MALLIN, D.N.B. (1976). Determination of benefin and trifluralin residues by quantitative gas-liquid chromatography /mass spectrometry. *J. Agric. Food Chem.* 24: 1223-1225.

- EDWARDS, C.A. (1989). Impact of herbicides on soil ecosystems. *Critical Reviews in Plant Sciences*. 8: 221-257.
- EMMERSON, J.L. and ANDERSON, R.C. (1966). Metabolism of trifluralin in the rat and dog. *Toxicol. Appl. Pharmacol.* 9: 84-97.
- FADOYOMI, O. and WARREN, G.F. (1977). Adsorption, desorption, and leaching of nitrofen and oxyfluorfen. *Weed Sci.* 25: 97-100.
- FARMER, W.J., IGUE, K., SPENCER, W.F. and MARTIN, J.P. (1972). Volatility of organochlorine insecticides from soil: 1. Effect of concentration, temperature, air flow rate, and vapour pressure. *Soil Sci. Soc. Amer. Proc.* 36: 443-447.
- FINE, D.H., KRULL, I.S., ROUNBEHLER, D.P., EDWARDS, G.S. and FOX, J.G. (1980). N-nitroso compound impurities in consumer and commercial products. In: *Dynamics, exposure and hazard assessment of toxic chemicals* (Ed. R. HAQUE). pp 417-423. Ann Arbor Science, Ann Arbor.
- FLETCHER, W.W. and KIRKWOOD, R.C. (1982). *Herbicides and plant growth regulators*. Granada, London.
- GILLETT, J.W. (1980). Terrestrial microcosm technology in assessing fate, transport and effects of toxic chemicals. In: *Dynamic, exposure, and hazard assessment of toxic chemicals* (Ed. R. HAQUE). pp 231-249. Ann Arbor Science, Ann Arbor.
- GLOTFELTY, D.E., TAYLOR, A.W., TURNER, B.C. and ZOLLER, W.H. (1984). Volatilization of surface-applied pesticides from fallow soil. *J. Agric. Food Chem.* 32: 638-643.
- GOLAB, T., ALTHAUS, W.A. and WOOTEN, H.L. (1979). Fate of [^{14}C] trifluralin in soil. *J. Agric. Food Chem.* 27: 163-179.
- GOLAB, T., HERBERG, R.J., DAY, E.W., RAUN, A.P., HOLZER, F.J. and PROBST, G.W. (1969). Fate of Carbon-14 trifluralin in artificial rumen fluid and in ruminant animals. *J. Agric. Food Chem.* 17: 576-580.
- GOLAB, T., HERBERG, R.J., GRAMLICH, J.V., RAUN, A.P. and PROBST, G.W. (1970). Fate of benefin in soils, plants, artificial rumen fluid, and the ruminant animals. *J. Agric. Food Chem.* 18: 838-844.
- GOLAB, T. and OCCOLOWITZ, J.L. (1979). Soil degradation of trifluralin mass spectrometry of products and potential products. *Biomed. Mass Spectro.* 6: 1-9.
- GOLAB, T., HERBERG, R.J., PARKA, S.J. and TEPE, J.B. (1967). Metabolism of carbon-14 trifluralin in carrots. *J. Agric. Food Chem.* 15: 638-641.
- GORING, C.A.I. and HAMAKER, J.W. (1972). *Organic chemicals in the soil environment*. Marcel Dekker INC., New York.
- GREAVES, R.C., BARKLEY, R.M. and SIEVERS, R.E. (1985). Rapid sampling and analysis of volatile constituents of airborne particulate matter. *Anal. Chem.* 57: 2807-2815.

- GROVER, R. SMITH, A.E., SHEWCHUCK, S.R., CESSNA, A.J. and HUNTER, J.H. (1988). Fate of trifluralin and triallate applied as a mixture to a wheat field. *J. Environ. Qual.* 17: 543-550.
- GUTH, J.A. (1980). The study of transformation s. In: *Interactions between herbicides and the soil* (Ed. R.J. HANCE). pp 123-157. Academic Press, London.
- HAIDER, K. (1983). Anaerobic microsites in soils and their possible effect on pesticide degradation. In: *Pesticide chemistry: Human welfare and environment*, Vol. 3, Mode of action, metabolism and toxicology (Ed. S. MATSUNAKA, D.H. HUTSON and S.D. MURPHY). pp 351-356. Pergamon Press, Oxford.
- HANCE, R.J. (1980). Transport in the vapour phase. In: *Interactions between herbicides and soil* (Ed. R.J. HANCE). PP 59-81. Academic Press, London.
- HAQUE, R. and FREED, V.H. (1975). *Environmental dynamic of pesticides*. Plenum Press, New York.
- HARISON, R.M. and ANDERSON, O.E. (1970). Soil analysis of trifluralin: Methodology and factors affecting quantitation. *Agron. J.* 62: 778-781.
- HARPER, L.A., WHITE, A.W. Jr., BRUCE, R.R., THOMAS, A.W. and LEONARD, R.A. (1976). Soil and microclimate effects on trifluralin volatilization. *J. Environ. Qual.* 5: 236-242.
- HARVEY, J. Jr. (1983). The fate of pesticide plant metabolites in vertebrates. In: *Pesticide chemistry: Human welfare and the environment*, Vol. 3, Mode of action, metabolism and toxicology (Ed. S. MATSUNAKA, D.H. HUTSON and S.D. MURPHY). pp 369-374. Pergamon Press, Oxford.
- HATZIOS, K.K. and PENNER, D. (1982). *Metabolism of herbicides in higher plants*. Burgess, Minneapolis.
- HAYES, M.H.B. (1976). Physical processes involved in the adsorption of pesticides at soil surfaces. In: *Proceeding of symposium of the persistence of insecticides and herbicides*, 22nd-24th March, 1976. pp 91-107. University of Reading.
- HEIKES, D.L. (1985). Purge and trap method for determination of ethylene dibromide in table-ready foods. *J. Assoc. Off. Anal. Chem.* 68: 431-436.
- HEIKES, D.L. (1987). Purge and trap method for determination of volatile halocarbons and carbon disulfide in table-ready foods. *J. Assoc. Off. Anal. Chem.* 70: 215-226.
- HEIKES, D.L. and HOPPER, M.L. (1986). Purge and trap method for determination of fumigants in whole grains, milled grain products, and intermediate grain-based foods. *J. Assoc. Off. Anal. Chem.* 69: 990-998.

- HEPLER, P.K. and JACKSON, W.T. (1969). Isopropyl N-phenylcarbamate affects spindle microtubule orientation in dividing endosperm cells of *Haemanthus katherinae* Baker. *J. Cell Sci.* 5: 727-743.
- HERCK, H.d'A., DYER, R.L., SCOTT, A.C. and ANBAR, M. (1977). Determination and disposition of trifluralin in the rat. Separation by sequential high-pressure liquid chromatography and quantitation by field ionization mass spectrometry. *J. Agric. Food Chem.* 25: 901-908.
- HERTEL, C., QUADER, H., ROBINSON, D.G. and MARME, D. (1980). Anti-microtubular herbicides and fungicides affect Ca^{2+} transport in plant mitochondria. *Planta.* 149: 336-340.
- HESEN, J.C. (1981). Storage and quality of potatoes. In: EAPR survey papers, 8th triennial conference of the European Association for Potato Research, 30 August-4 September 1981. pp 123-132. Mnchen.
- HESS, F.D. (1983). Mode of action of herbicides that affect cell division. In: *Pesticide chemistry: Human welfare and the environment*, Vol.3 Mode of action, metabolism and toxicology (Ed. S. MATSUNAKA, D.H. HUTSON and S.D. MURPHY). pp 79-84. Pergamon Press, Oxford.
- HESS, F.D. (1989). Herbicide interference with cell division plants. In: *Target sites of herbicide action* (Ed. P. BOGER and G. SANDMANN). pp 85-103. CRC Press, INC., Florida.
- HESS, F.D. and BAYER, D.E. (1974). The effect of trifluralin on the ultrastructure of dividing cells of the root meristem of cotton (*Gossypium hirsutum* L. 'Acala 4-42'). *J. Cell Sci.* 15: 429-441.
- HESS, F.D. and BAYER, D.E. (1977). Binding of the herbicide trifluralin to *Chlamydomonas* flagellar tubulin. *J. Cell Sci.* 24: 351-360.
- HILL, I.R. (1978). Microbial transformation of pesticides. In: *Pesticide microbiology* (Ed. I.R. HILL and S.J.L. WRIGHT). pp 137-202. Academic Press, London.
- HILL, I.R. and WRIGHT, S.J.L. (1978). The behaviour and fate of pesticides in microbial environments. In: *Pesticide microbiology* (Ed. I.R. HILL and S.J.L. WRIGHT). pp 79-136. Academic Press, London.
- HILTON, J.L. (1972). Lipid role in selective action of trifluralin. 132 Abstr. 13th Meeting of Weed Sci. Am., St. Louis, 1972.
- HILTON, J.L. and CHRISTIANSEN, M.N. (1972). Lipid contribution to selective action of trifluralin. *Weed Sci.* 20: 290-294.
- HOLLINGSWORTH, E.B. (1980). Volatility of trifluralin from field soil. *Weed Sci.* 28: 224-228.
- HOLLIST, R.L. and FOY, C.L. (1971). Trifluralin interactions with soil constituents. *Weed Sci.* 19: 11-16.

- HOLZER, F.J., SCROGGS, R.E. and LEARY, J.B. (1963). Determination of trifluralin in formulation. *J. Assoc. Off. Anal. Chem.* 46: 659-662.
- HOROWITZ, M., HULIN, N. and BLUMENFELD, T. (1974). Behaviour and persistence of trifluralin in soil. *Weed Res.* 14: 213-220.
- HOWARD, H.W. (1972). Botany of the crop. In: *Potatoes: a manual for farmers and advisors*. pp 11-14. Harston, Cambridge.
- HURLE, K. and WALKER, A. (1980). Persistence and its prediction. In: *Interactions between herbicides and the soil* (Ed. R.J. HANCE). pp 83-122. Academic Press, London.
- IGUE, K., FARMER, W.J., SPENCER, W.F. and MARTIN, J.P. (1972). Volatility of organochlorine insecticides from soil: Effect of relative humidity and soil water content on dieldrin volatility. *Soil Sci. Amer. Proc.* 36: 447-450.
- IVIE, G.W. and CASIDA, J.E. (1971). Photosensitizers for the accelerated degradation of chlorinated cyclodienes and other insecticide chemicals exposed to sunlight on bean leaves. *J. Agric. Food Chem.* 19: 410-416.
- KATZ, S.E., FASSBENDER, C.A. and STRUSZ, R.F. (1969). Studies on the possible formation of azo compounds in rumen fluid. *J. Assoc. Off. Anal. Chem.* 52: 1213-1220.
- KAUFMAN, D.D. (1976). Phenols. In: *Herbicides: Chemistry, degradation, and mode of action*, Vol. 2, (Ed. P.C. KEARNEY and D.D. KAUFMAN). pp 665-708. Marcel Dekker, INC., New York.
- KEARNEY, P.C. and KONTSON, A. (1976). A simple system to simultaneously measure volatilization and metabolism of pesticides from soils. *J. Agric. Food Chem.* 24: 424-426.
- KEARNEY, P.C., PLIMMER, J.R., WHEELER, W.B. and KONTSON, A. (1976). Persistence and metabolism of dinitroaniline herbicides in soils. *Pest. Biochem. Physiol.* 6: 229-238.
- KENAGA, E.E. (1972). Guidelines for environmental study of pesticides determination of bioconcentration potential. *Residue Rev.* 44: 73-113.
- KENNEDY, J.M. and TALBERT, P.E. (1977). Comparative persistence of dinitroaniline type herbicides on the soil surface. *Weed Sci.* 25: 373-381.
- KETCHERSID, M.L., BOSELL, T.E. and MERKLE, M.G. (1969). Uptake and translocation of substituted aniline herbicides in peanut seedlings. *Agron. J.* 61: 185-187.
- KHAN, M.Q. (1987). Ph.D. thesis, University of Glasgow.
- KLINGMAN, G.C., ASHTON, F.M. and NOORDHOFF, L.J. (1975). Dinitroaniline. In: *Weed science: Principles and practices* (Ed. G.C. KLINGMAN, F.M. ASHTON and L.J. NOORDHOFF). pp 188-199. John Wiley and Sons, New York.

- KNSLI, E. (1979). Objective and strategies of world food production. In: *Advances in pesticide science, Part 1, Vol. 1* (Ed. H. GEISSBLER). pp 5-14. IUPAC, Pergamon Press, Oxford.
- KOEMAN, J.H. (1979). Chemical in the environment and their effects on ecosystems. In: *Advances in pesticide science, Part 1, Vol. 1* (Ed. H. GEISSBLER). pp 25-38. IUPAC, Pergamon Press, Oxford.
- KRAISH, A.-S.F. (1980). M.Sc. thesis, University of Alexandria.
- KULSHRESTHA, G. and MUKERJEE, S.K. (1986). The photochemical decomposition of the herbicide isoproturon. *Pest. Sci.* 17: 489-494.
- LEISTRA, M. (1980). Transport in solution. In: *Interactions between herbicides and the soil* (Ed. R.J. HANCE). pp 31-58. Academic Press, London.
- LEITIS, E. (1973). Ph.D. dissertation, University of California, Davis.
- LEITIS, E. and CROSBY, D.G. (1974). Photodecomposition of trifluralin. *J. Agric. Food Chem.* 22: 842-848.
- LEONARD, M.J. (1988). Ph.D. thesis, University of Glasgow.
- LEONARD, M.J. and MCGEE, E., JARVIS, M.C. and DUNCAN, H.J. (1986). The effect of sprout suppressant chemicals on wound healing. In: *Aspects of Applied Biology 13, Crop protection of sugar beet and crop protection and quality of potatoes*. pp 481-490.
- LIGOCKI, M.R. and PANKOW, J.F. (1985). Assessment of adsorption/solvent extraction with polyurethane foam and adsorption/desorption with Tenax-GC for the collection and analysis of ambient organic vapours. *Anal. Chem.* 57: 1138-1144.
- LYKKEN, L. (1972). Role of photosensitizers in alteration of pesticide residues in sunlight. In: *Environmental toxicology of pesticides* (Ed. F. MATSUMURA, G.M. BOUSH and T. MISATO). pp 449-469. Academic Press, New York.
- MARTH, P.C. and SCHULTZ, E.S. (1950). Effect of growth regulators on sprouting of stored table stock potatoes and on waste piles for control of diseases. *Amer. Pot. J.* 27:23-32.
- MARCHETERRE, L., CHOUDHRY, G.G. and WEBSTER, G.R.B. (1988). Environmental photochemistry of herbicides. *Residue Rev.* 103: 61-126.
- McCLENNY, W.A., PLEIL, J.D., HOLDREN, M.W. and SMITH, R.N. (1984). Automated cryogenic preconcentration and gas chromatographic determination of volatile organic compounds in air. *Anal. Chem.* 56: 2947-2951.
- MCGEE, E. (1984). Ph.D. thesis, University of Glasgow.

- McGEE, E., JARVIS, M.C. and DUNCAN, H.J. (1986). The relationship between temperature and sprout growth in stored seed potatoes. *Pot. Res.* 29: 521-524.
- McGEE, E., JARVIS, M.C. and DUNCAN, H.J. (1987). Effects of spectral distribution on suppression of sprout growth by light. *Abstr. 10th Trienn. Conf. EAPR.* pp 333-334.
- McKENZIE, J. (1989). Ph.D. thesis, University of Glasgow.
- McMAHON, R.E. (1966). The photochemical demethylation of N-methyl-2,6-dinitro-4-trifluoromethyl aniline. A possible model for enzymatic dealkylation. *Tetra. Let.* 21: 2307-2310.
- MEIGH, D.F., FILMER, A.A.E. and SELF, R. (1973). Production of growth suppressing volatile substances by stored potato tubers. II Growth inhibitory volatile aromatic compounds produced by Solanum tuberosum. *Phytochem.* 12: 987-993.
- MESSERSMITH, C.G., BURNSIDE, O.C. and LAVY, T.L. (1971). Biological and non-biological dissipation of trifluralin from soil. *Weed Sci.* 19: 285-290.
- METCALF, R.L. (1977). Model ecosystem approach to insecticide degradation: a critique. *Ann. Rev. Entomol.* 22: 241-261.
- MIEURE, J.P. and DIETRICH, M.W. (1973). Determination of trace organics in air and water. *J. Chromatographi c Sci.* 11: 559-570.
- MILL, T. (1980). Data needs to predict the environmental fate of organic chemicals. In: *Dynamics, exposure and hazard assessment of toxic chemical* (Ed. R. HAQUE). pp 297-322. Ann Arbor Science, Ann Arbor, Mich.
- MILLER, J.H., KEELEY, P.E., CARTER, C.H. and THULLEN, R.J. (1975). Soil persistence of trifluralin, benefin, and nitralin. *Weed Sci.* 23: 211-214.
- MILLER, G.C. and ZEPP, P.G. (1983). Extrapolating photolysis rates from the laboratory to the environment. *Residue Rev.* 85: 89-110.
- MOILANEN, K.W., CROSBY, D.G., SODERQUIST, C.J. and WONG, A.S. (1975). Dynamic aspects of pesticide photodecomposition. In: *Environmental Dynamics of pesticides* (Ed. R. HAQUE and V.H. FREED). pp 45-60. Plenum Press, New York.
- MONGAR, K. and MILLER, G.C. (1988). Vapour phase photolysis of trifluralin in an outdoor chamber. *Chemosphere* 17: 2183-2188.
- MOYER, J.R. and ELDER, J.L. (1984). Quantitative confirmation of ethalfluralin and trifluralin in soil extracts by negative chemical ionization mass spectrometry. *J. Agric. Food Chem.* 32: 866-868.
- MUIR, J.W., BOYD, I.M.G. and DUNCAN, H.J. (1987). A comparison of the effect of irradiation and chemical sprout suppressants on sugar levels in tubers. *Abstr. 10th Trienn. Conf. EAPR.* pp 164-165.

- NASH, M.J. (1978). Crop conservation and storage in cool temperate climates. Pergamon Press, Oxford.
- NASH, R.G. (1983). Comparative volatilization and dissipation rates of several pesticides from soil. *J. Agric. Food Chem.* 31: 210-217.
- NEELY, W.B. (1980). A method for selecting the most appropriate environmental experiments on a new chemical. In: Dynamics, exposure and hazard assessment of toxic chemical (Ed. R. HAQUE). pp 287-296. Ann Arbor Science, Ann Arbor, Mich.
- NEGI, N.S. and FUNDERBURK, H.H. (1966). Effect of solutions and vapours of trifluralin on growth of roots and shoots. *Weed Sci. Soc. Amer. Abstr.* pp 37-38.
- NEWMAN, J.F. (1978). Pesticides. In: Pesticide microbiology (Ed. I.R. HILL and S.J.L. WRIGHT). pp 1-16. Academic Press, London.
- NILLES, G.P. and ZABIK, M.J. (1974). Photochemistry of bioactive compounds. Multiphase photodegradation of basalins. *J. Agric. Food Chem.* 22: 684-688.
- O'HAGAN, N., BOYD, I.M.G. and DUNCAN, H.J. (1987). Studies on dimethylnaphthalene (DMN) analogues and their activities as sprout suppressant chemicals. *Abstr. 10th Trienn. Conf. EAPR.* pp 335-336.
- ONUSKA, F.I. and KARASEK, F.W. (1984). Open tubular column gas chromatography. In: Environmental Sciences (Ed.). pp Plenum Press, New York.
- OSGERBY, J.M. (1973). Processes affecting herbicide action in soil. *Pest. Sci.* 4: 247-258.
- OTSON, R., LEACH, J.M. and CHUNG, L.T.K. (1987). Sampling of airborne polycyclic aromatic hydrocarbons. *Anal. Chem.* 59: 1701-1705.
- OTTER, R.J. (1988). Pesticides in the aquatic environment-data needs for their control. In: Risk assessment of chemicals in the environment (Ed. M.L. Richardson). pp 481-532. The Royal Society of Chemistry, Burlington House,
- PANKOW, J.F. and KRISTENSEN, T.J. (1983). Effects of flow rate and temperature on thermal desorption of polycyclic aromatic hydrocarbons and pesticides from Tenax-GC. *Anal. Chem.* 25: 2187-2192.
- PARKA, S.J. and SOPER, O.F. (1977). The physiological and mode of action of the dinitroaniline herbicides. *Weed Sci.* 25: 79-87.
- PARKA, S.J. and TEPE, J.B. (1969). The disappearance of trifluralin from field soils. *Weed Sci.* 17: 119-122.
- PAROCHETTI, J.V., DEC, Jr.G.W. and BURT, G.W. (1976). Volatility of eleven dinitroaniline herbicides. *Weed Sci.* 24: 529-532.

- PAROCHETTI, J.V. and HEIN, E.R. (1973). Volatility and photodecomposition of trifluralin, benefin, and nitralin. *Weed Sci.* 21: 469-473.
- PAROCHETTI, J.V. and WARREN, G.F. (1966). Vapour losses of IPC and CIPC. *Weeds* 14: 281-285.
- PARR, J.F. and SMITH, S. (1973). Degradation of trifluralin under laboratory conditions and soil anaerobiosis. *Soil Sci.* 155: 55-63.
- PAULSON, G.D. (1975). Metabolic fates of herbicides in animals. *Residue Rev.* 58: 1-106.
- PAYNE, Jr.W.R., POPE, Jr.J.D. and BENNER, J.E. (1974). An integrated method for trifluralin, diphenamid, and paraquat in soil and runoff from agricultural land. *J. Agric. Food Chem.* 22: 79-82.
- PELLIZZARI, E.D., BUNCH, J.E., CARPENTER, B.H. and SAWICKI, E. (1975a). Collection and analysis of trace organic vapour pollutants in ambient atmospheres. Technique for evaluating concentration of vapours by sorbent media. *Environ. Sci. Tech.* 9: 552-555.
- PELLIZZARI, E.D., CARPENTER, B.H., BUNCH, J.E. and SAWICKI, E. (1975b). Collection and analysis of trace organic vapour pollutants in ambient atmosphere. Thermal desorption of organic vapours from sorbent media. *Environ. Sci. Tech.* 9: 556-560.
- PLIMMER, J.R. (1970). The photochemistry of halogenated herbicides. *Residue Rev.* 1: 47-74.
- PLIMMER, J.R. (1972). Principles of photodecomposition of pesticides. In: *Degradation of synthetic organic molecules in the biosphere* (Proceedings of a conference, June 12-13, 1971, San Francisco, California). National Academy of Sciences, Washington.
- PLIMMER, J.R. (1976). Volatility. In: *Herbicides, chemistry, degradation, and mode of action*, Vol. 2 (Ed. P.C. KEARNEY and D.D. KAUFMAN). pp 891-934. Marcel Dekker, INC., New York.
- PLIMMER, J.R. and KLINGEBIEL, U.I. (1974). Photochemistry of N-sec-butyl-4-tert-butyl-2,6-dinitroaniline. *J. Agric. Food Chem.* 22: 689-693.
- PONNAMPALAM, R. and MONDY, N.I. (1986). The effect of sprout inhibitor isopropyl N-(3-chlorophenyl) carbamate (CIPC) on phenolic acids and ascorbic acid content of potatoes. *J. Agric. Food Chem.* 34: 262-263.
- POOLE, C.F. and SCHUETTE, S.A. (1984). *Contemporary practice of chromatography*. Elsevier Science Publishers B.V., Amsterdam.
- PROBST, G.W., GOLAB, T., HERBERG, R.J., HOLZER, F.J., PARKA, S.J., VAN DER SCHANS, C. and TEPE, J.B. (1967). Fate of trifluralin in soils and plants. *J. Agric. Food Chem.* 15: 592-599.

- PROBST, G.W., GOLAB, T., and WRIGHT, W.L. (1976). Dinitroaniline s. In: *Herbicides: Chemistry, degradation, and mode of action*, Vol. 1 (Ed. P.C. KEARNEY and D.D. KAUFMAN). pp 453-500. Marcel Dekker, INC., New York.
- PROBST, G.W. and TEPE, J.B. (1969). Trifluralin and related compounds. In: *Degradation of herbicides* (Ed. P.C. KEARNEY and D.D. KAUFMAN). pp 255-282. Marcel Dekker INC., New York.
- RILEY, D. (1976). Physical loss and redistribution of pesticides in the liquid phase. In: *The persistence of insecticides and herbicides* (Proc. Symposium, 22nd-24th March 1976, at the University of Reading). pp 109-115. British Crop Protection Concil.
- RHODES, R.C., BELASCO, I.J., and PEASE, H.L. (1970). Determination of mobility and adsorption of agrichemicals on soils. *J. Agric. Food Chem.* 18: 524-528.
- RHODES, A., SEXON, W.A., SPENCER, L.G. and TEMPLEMAN, W.G. (1950). Isopropylphenyl carbamate to reduce sprouting of potato tubers during storage. *Research* 3: 189-190.
- ROSEN, J.D. (1972). The photochemistry of several pesticides. In: *Environmental toxicology of pesticides* (Ed. F. MATSUMURA, G.M. BOUSH and T. MISATO). pp 435-447. Academic Press, New York.
- ROSS, R.D., MORRISON, J., ROUNBEHLER, D.P., FAN, S. and FINE, D.H. (1977). N-Nitroso compound impurities in herbicide formulations. *J. Agric. Food Chem.* 25: 1416-1418.
- SAGAR, G.R., CASELEY, J.C., KIRKWOOD, R.C. and PAKER, C. (1982). Herbicides in plants. In: *Weed control handbook: Principles* (Ed. H.A. ROBERTS). pp 64-86. Blackwell Scientific Publication, Oxford.
- SAVAGE, K.E. (1973). Nitralin and trifluralin persistence in soil. *Weed Sci.* 21: 285-288.
- SAVAGE, K.E. and BARRENTINE, W.L. (1969). Trifluralin persistence as affected by depth of soil incorporation. *Weed Sci.* 17: 349-352.
- SAVAGE, K.E. and JORDAN, T.N. (1980). Persistence of three dinitroaniline herbicides on the soil surface. *Weed Sci.* 28: 105-110.
- SEIBER, J.N., WOODROW, J.E., SHAFIK, T.M. and ENOS, H.F. (1975). Determination of pesticides and their transformation products in air. In: *Environmental dynamics of pesticides* (Ed. R. HAQUE and V.H. FREED). pp 17-43. Plenum Press, New York.
- SMITH, A.E. (1981). Comparison of solvent systems for extraction of atrazine, benzoxyprop, flamprop and trifluralin from weathered field soils. *J. Agric. Food Chem.* 29: 111-115.

- SMITH, A.E. and MUIR, D.C.G. (1984). Determination of extractable and nonextractable radioactivity from small field plots 45 and 95 weeks after treatment with [^{14}C] dicamba, (2,4-dichloro[^{14}C]p henoxyl)acetic acid, [^{14}C] triallate, and [^{14}C]trifluralin in. J. Agric. Food Chem. 32: 588-593.
- SMITH, A.E. and MUIR, D.C.G. (1984). Determination of extractable and nonextractable radioactivity from small field plots 45 and 95 weeks after treatment with [^{14}C] triallate, and [^{14}C] trifluralin. J. Agric. Food Chem. 32: 588-593.
- SODERQUIST, C.J., CROSBY, D.G., MOILANEN, K.W., SEIBER, J.N. and WOODROW, J.E. (1975). Occurrence of trifluralin and its photoproducts in air. J. Agric. Food Chem. 23: 304-309.
- SOLBAKKEN, E., HOLE, H., LODE, O. and PEDERSEN, T.A. (1982). Trifluralin persistence under two different soil and climatic conditions. Weed Res.. 22: 319-328.
- SOMERVILLE, L. (1988). Studies on the fate of chemicals in the environment with particular reference to pesticides. In: Risk assessment of chemicals in the environment (Ed. M.L. RICHARDSON). pp 451-480. The Royal Society of Chemistry, Burlington House, London.
- SPENCER, W.F. and CLIATH, M.M. (1973). Pesticide volatilization as related to water loss from soil. Environ. Qual. 2: 284-289.
- SPENCER, W.F. and CLIATH, M.M. (1974). Factors affecting vapour loss of trifluralin from soil. J. Agric, Food Chem. 22: 987-991.
- SPENCER, W.F. and CLIATH, M.M. (1976). The solid-air interface: Transfer of organic pollutants between the solid and air phases. In: Advances in environmental science and technology, Part 1 (Ed. I.H. SUFFET). pp107-126. John Wiley, New York.
- SPENCER, W.F., CLIATH, M.M. and FARMER, W.J. (1969). Vapour density of soil-applied dieldrin as related to soil-water content, temperature, and dieldrin concentration. Soil Sci. Soc. Am. Proc. 33: 509-511.
- SPENCER, W.F., FARMER, W.J. and CLIATH, M.M. (1973). Pesticide volatilization. Residue Rev. 49: 1-47.
- SPENCER, W.F. and FARMER, W.J. (1980). Assessment of the vapour behaviour of toxic organic chemicals. In: Dynamics, exposure and hazard assessment of toxic chemicals (Ed. R. HAQUE). pp 143-161. Ann Arbor Science, Ann Arbor, Mich.
- STEPHEN, N.H. and DUNCAN, H.J. (1984). Potato sprout suppressant activity of some substituted naphthalenes. Abstr. 9th Trienn. Conf. EAPR. pp 321-322.
- STRANG, R.H. and ROGERS, R.L. (1971). A microradiographic study of ^{14}C -trifluralin absorption. Weed Sci. 19: 363-369.

- SULLIVAN, R.G., KNOCHE, H.W. and MARKLE, J.C. (1980). Photolysis of trifluralin: Characterization of azobenzene and azoxybenzene photodegradation products. *J. Agric. Food Chem.* 28: 746-755.
- SUNTIO, L.R., SHIU, W.Y., MacKAY, D., SEIBER, J.N. and GLOTFELTY, D. (1988). Critical review of Henry's Law Constant for pesticides. *Residue Rev.* 103: 1-51.
- SWANN, C.W. and BEHRENS, R. (1972). Phytotoxicity of trifluralin vapours from soil. *Weed Sci.* 20: 143-146.
- TALBERT, R.E. (1965). Effects of trifluralin on soybean root development. In: *Proc. 18th Annual Meeting Southern Weed Conf.* pp 652.
- TALEKAR, N.S. and LICHTENSTEIN, E.P. (1972). Effects of metabolic inhibitors, aeration, and other factors on penetration and translocation of lindane in pea plants. *J. Agric. Food Chem.* 20: 1260-1263.
- TEPE, J.B. and SCROGGS, R.E. (1967). Trifluralin. In: *Analytical methods for pesticides, plant growth regulators, and food additives. Vol.V, Additional principles and methods of analysis* (Ed. G.ZWEIG). pp527-535. Academic Press, New York.
- TORSTENSSON, L. (1980). Role of microorganisms in decomposition. In: *Interactions between herbicides and the soil* (Ed. R.C. HANCE). pp 159-178. Academic Press, London.
- UPADHYAYA, M.K. and NOODEN, L.D. (1977). Mode of dinitroaniline herbicide action. I. Analysis of the colchicine-like effects of dinitroaniline herbicides. *Plant Cell Physiol.* 18: 1319-1330.
- UPCHURCH, R.P. (1966). Behaviour of herbicides in soil. *Residue Rev.* 16: 46-85.
- VANDEVENTER, J.W., MEGGITT, W.F. and PENNER, D. (1986). Absorption, translocation and metabolism of ethalfluralin and trifluralin in Solanum spp. *Pest. Sci.* 17: 380-384.
- VAN DYK, L.P. and VISWESWARIAH, K. (1974). Pesticides in air: Sampling methods. *Residue Rev.* 15: 91-134.
- WALKER, A., BRIGGS, G.G., GREAVES, M.P., HANCE, R.J. and THOMPSON, A.R. (1982). Herbicides in soil. In: *Weed control handbook: Principles* (Ed. H.A. ROBERTS). pp 87-105. Blackwell Scientific Publications, Oxford.
- WALLACE, K., GROVER, R. and WESTCOTT, N. (1988). Evaluation of an activated carbon filter for the retention of selected pesticide vapours. *J. Environ. Sci. Health B23*: 605-621.
- WAMPLER, T.P., BOWE, W.A. and LEVY, E.J. (1985). Dynamic headspace analysis of residual volatiles in pharmaceuticals. *J. Chrom. Sci.* 23: 64-67.

- WHEATLEY, G.A. (1976). Physical loss and redistribution of pesticides in the vapour phase. In: Persistence of insecticides and herbicides (Proc. Symposium, 22nd-24th March 1976, at the University of Reading). pp 117-125. British Crop Protection Council.
- WHEELER, W.B., STRATTON, G.D., TWILLEY, R.R., OU, L.-T., CARLSON, D.A. and DAVIDSON, J.M. (1979). Trifluralin degradation and binding in soil. J. Agric. Food Chem. 27: 702-706.
- WILLIAMS, P.P. and FEIL, V.J. (1971). Identification of trifluralin metabolites from rumen microbial cultures. Effect of trifluralin on bacteria and protozoa. J. Agric. Food Chem. 19: 1198-1204.
- WOODROW, J.E., CROSBY, D.G., MAST, T., MOILANEN, K.W. and SEIBER, J.N. (1978). Rates of transformation of trifluralin and parathion vapours in air. J. Agric. Food Chem. 26: 1312-1316.
- WORTH, H.M. (1968). The toxicologic evaluation of benefin and trifluralin. Industrial Medicine and Surgery. 37: 545.
- WORTHING, C.R., RICHARDSON, W.G. and TAYLOR, W.A. (1982). Herbicides and their properties. In: Weed control handbook: Principles (Ed. H.A. ROBERTS). pp 106-157. Blackwell Scientific Publications, Oxford.
- WRIGHT, W.L. and WARREN, G.F. (1965). Photochemical decomposition of trifluralin. Weeds 13: 329-331.
- YOON, J.S., MASON, J.M., VALENCIA, R., WOODRUFF, R.C. and ZIMMERING, S. (1985). Chemical mutagenesis testing in Drosophila. IV. Results of 45 coded compounds tested for the National Toxicology Program. Environ. Mutagen. 7: 349-367.
- ZAKI, M. and REYNOLDS, H.T. (1961). Effects of various soil types and methods of application upon uptake of three systemic insecticides by cotton plants in the greenhouse. J. Econ. Entom. 54: 568-572.
- ZEPP, R.G. and CLINE, D.M. (1977). Rates of direct photolysis in aquatic environment. Environ. Sci. Technol. 4: 359-
- ZIMDAHL, R.L. and GWYNN, S.M. (1977). Soil degradation of three dinitroaniline s. Weed Sci. 25: 247-251.

